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AND

PRACTICAL CRYSTAL MEASUREMENT

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CRYSTALLOGRAPHY

AND

PRACTICAL CRYSTAL MEASUREMENT

BY

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THE optical part of a crystallographic investigation has in the past unfortunately been very frequently omitted, partly because of the experimental difficulties in the way of a study of the optics of so small an object as a crystal, especially if it be one of a chemically prepared substance, and partly because of the necessary knowledge of the optical properties of crystals having been more difficult to acquire than skill in the use of the goniometer. Very numerous measurements of crystals have been published without any reference whatever to their optical properties, and still more in which the reference is a very brief, cursory, and altogether inadequate one. Now the optical characters of crystals are of vital importance, for a knowledge of them is frequently essential in order that we may be able to decide definitely as to which particular system or class of symmetry is present; in many complicated cases more or less doubt is left by the goniometrical investigation, which the determination of the optical properties of the crystals is able to remove entirely. Moreover, the behaviour of light in its passage through a crystal affords a valuable indication of the nature of the internal structure, that is, of the particular point-system, not merely the space-lattice, in accordance with which the crystal edifice is erected. Further, the optical properties are often so eminently characteristic, in their details, of a specific crystalline substance, that they may be trustworthily relied upon and conveniently employed for the identification of the substance; and often this happens in cases where goniometrical investigation would be very troublesome, on account of the unsuitability of the crystals for use on the goniometer, by reason of their imperfect faces, the presence of striation, ready decomposition, or weathering, or other form of exterior deterioration. In such cases the optical investigation, being more or less independent of the nature of the exterior faces, is simply invaluable. In fine, a discussion of the optical characters, and a table of the optical constants, are essential parts of any complete description of the crystals of a substance.

The main operations comprised in the practical investigation of the

optical properties of a crystalline substance are in general three in number, and are as follows :

(1) We have to determine the positions of the three principal (mutually rectangular) axes of the optical ellipsoid ; that is, the orientation of that imaginary ellipsoid within the crystal which we have seen in Chapter XXXI. is the expression of the optical properties (just as a similar, but not necessarily identical, ellipsoid is capable of expressing the distribution of the property of cohesion), and the orientation and character of which depend both on the nature of the space-lattice of the homogeneous molecular structure, and on the specific nature of the particular substance itself. This determination is carried out by studying the behaviour of the crystal in parallel polarised light, and especially by ascertaining its extinction directions in the dark field of the polariscope.

(2) We have to ascertain the relative lengths of the three rectangular axes of the optical ellipsoid, and to do so we determine the refractive index of the crystals, that is, their power of bending the rays of light, along each of the three axial directions which we have ascertained as the result of (1).

(3) We independently confirm the results of (1) and (2), as well as amplify the information, by studying the optical interference phenomena displayed by the crystals in convergent polarised light, and, in the event of the crystal proving to possess two optic axes by exhibiting a biaxial interference figure of spectrum-coloured lemniscates and dark hyperbolic "brushes," measuring the angle of separation of the so-called "optic axes" marked by the vertices of the two brushes. The optic axes are quite distinct from the axes of the optical ellipsoid, but dependent on the relative lengths of those axes, and have been preliminarily explained in Chapter XXXI. in connection with the properties of the space-lattices. When the crystal only possesses a single optic axis, the circular concentric character of the rings of the interference figure, and an unalterable rectangular dark cross radiating from the centre and which never separates into hyperbolæ, at once reveals the fact. Incidentally operation (3) affords us quite a number of phenomena in which the crystalline substance can display its individuality. Moreover, when a uniaxial interference figure is exhibited the crystal must belong to the tetragonal, hexagonal, or trigonal system ; and when a biaxial figure is afforded the crystal must be of rhombic, monoclinic, or triclinic symmetry. These facts alone would enable us to decide on the true crystal system, in a case such as that of our typical crystal of potassium sulphate, which while really rhombic is of pseudo-hexagonal habit, and indeed within a few minutes of truly hexagonal morphology. The fact that potassium sulphate affords a biaxial interference figure is a decisive proof of rhombic symmetry, and would be so, even if adequately good crystals for accurate measurement and determination of the slight deviation from 60° had never been obtained.

In order to render the meaning of these three operations fully intelligible and clear, and to understand thoroughly the behaviour of crystals towards light rays, it will be advisable to review briefly the fundamental

facts, first as to the nature of the agent, light, that we are employing, a subject which recent research has rendered of especial interest at the present time, and secondly, in the next few chapters, of crystal optics. Optical crystallography often looks so appallingly difficult to a beginner, that it has been felt desirable by the author to state thus at once, in these introductory pages, that the experimental work is really of a very simple character, essentially ranging around the three operations above specified. Not only is this department of the crystallographer's work straightforward and easy, provided he thoroughly understands what he is doing and that the proper instruments are available, but it is also fascinatingly interesting. For the phenomena of polarised light are admittedly the most beautiful which experimental science has yet afforded us, and the interference phenomena exhibited by crystals, and referred to above as requiring to be studied, are among the most superb of all those which even polarised light can provide.

Consequently, the optical part of a crystallographic investigation is of surpassing interest, and if at times the phenomena prove complicated and require most careful study, the results are not only themselves rendered the more valuable thereby, but the experimental means of arriving at them are intrinsically so beautiful as far more than to compensate for all the trouble involved.

The Nature of Light.

It is now an established fact that light, using the term in its objective sense, consists of a vibratory motion, or oscillatory change of condition, in an everywhere pervading medium, the ether, the vibrations or oscillations being of such a definitely periodic character, **transversely** to the line of propagation, as to produce waves or undulations the impact of which on the peculiarly sensitive layer of the retina of the eye gives rise, on transmission by the optic nerve to the brain, to the sensation which we term, subjectively, light. The motion has been advisedly stated to be "in" the medium rather than "of" the medium, for there have until recently been two forms of the undulatory theory, quite irrespective of the old emission theory favoured by Newton, which was definitely proved to be incorrect by Foucault, who found experimentally that the velocity of light in water is less than it is in air, whereas according to the theory based upon the emission of "light corpuscles" it should travel more rapidly in water than in air.

According to one, now abandoned, form of the undulatory theory, the waves of light are actual transverse vibrations of the ethereal medium itself, while according to the other and more recent and generally accepted form the vibrations are due to a rapid periodic change in the electrical and magnetic condition of the ether. Both forms of the wave theory postulate a transverse vibration or oscillation in the medium; they only differ as regards the manner of its production. The later form is distinguished as the electromagnetic theory of light, and is now receiving further confirmation every day. The mechanical form of the wave theory demands the propagation of longitudinal waves as well as transverse ones, and the existence of such longitudinal waves in rays of light has not been proved. The electromagnetic theory of light does not lead to the supposition of any but transverse vibrations, and from many other considerations, derived from the developments of the remarkable discoveries of the cathode and X-rays and of radium and radio-active substances, an account of which will be given later in this chapter, it is much more likely to represent the truth.

The Medium, Ether.—All the forms of energy with which we are acquainted

require media for their propagation. Thus sound requires a material substance, gaseous, liquid, or solid, for the propagation of its longitudinal vibrations, which are incomparably grosser than those of light. It is, in fact, this all but infinitely greater length of sound-waves which renders them apparently so much more capable of bending round an interposing object than the waves of light, although we now know, from the exquisite phenomena of diffraction spectra, that light-waves are equally able, considering their minute size, to bend round an edge of adequate sharpness. Sound, however, cannot be transmitted through a vacuum, while light travels not only unimpeded through empty space with enormous velocity, 185,400 miles per second —compared with which the 1100 feet per second of sound in air is an almost negligible quantity,—but with even greater velocity through space than through air or any other gaseous medium. The presence of matter does, indeed, exert more or less restraint on the vibrations of light, its velocity being more considerably reduced by its passage through transparent liquids and solids than through gases; yet even in the cases of highest resistance the velocity of light is immensely greater than that of sound. Ample proof of this reduction in velocity is afforded by the phenomena of refraction, or the bending of the rays of light by transparent material media, with which we shall have so much to do in studying the optical properties of crystals. This bending of the rays of light when they enter a transparent material substance from a vacuum, or when they pass from a lighter to a denser transparent medium, for instance, from oil into a diamond crystal, is one of the most characteristic properties of light vibrations, and is intimately connected with, and indeed a function of, the reduction in velocity.

The conception of an ether is not at first easy to grasp. It is difficult to conceive anything other than material substances, that is to say, the chemical elements, their compounds, and mechanical mixtures of either or both. It also requires the scientific use of the imagination to picture an everywhere existing medium which interpenetrates all material substances, besides filling interstellar space. Yet recent advances have rendered the conception far less difficult than it formerly was. We have seen that there are certainly intermolecular and probably interatomic spaces in the crystal edifice, and for that reason we do not speak of the structural ratios referred to in Chapter XXXI., the dimensions of the unit cell of the space-lattice, as the relative dimensions of the molecules, but as molecular distance ratios; for although they do represent the dimensions of the molecular or polymolecular cell or elementary parallelepipedon of the space-lattice of the crystal structure, that is, of the bricks of which the edifice is built up, yet we do not know how much of that space is occupied by matter and how much is free space. Moreover, we now know further, from the researches of Sir William Crookes, Sir J. J. Thomson, Sir E. Rutherford, and a rapidly growing band of other workers in the field which they have so wonderfully opened up, that the chemical atom itself is not entirely composed of matter, but of a positively electrified nucleus surrounded by a number of electronic negatively electrified corpuscles or "electrons" of negative electricity separated by free space; so that it is now quite easy to comprehend that what appears to be impenetrably solid matter is in reality anything but impervious and solid in the old sense of the word. It is far more difficult to believe in the possibility of action at a distance without any intervening medium, in the cases of light, magnetism, and gravitation, than to concede the existence of a medium, for which, moreover, the evidence every day becomes stronger. There can be little doubt that the influence of the sun on this earth, as on the other planets of the solar system, in constantly maintaining and reinforcing its energy, is due to the conveying power of the ethereal medium.

Of the properties of the ether we are not yet justified in stating anything. The promulgators of the earlier form of the undulatory theory assumed the ether to possess both elasticity and density, but the possibility of longitudinal vibrations in a medium so endowed, and their non-discovery experimentally, has rendered the sup-

position more than doubtful. The difficulty has been met by imagining the ether incompressible, which would so enhance the velocity of the longitudinal wave as to render it infinite. Moreover, it has been pointed out that all that the ether requires is torsional rigidity, or resistance to change of shape, the characteristic property of a jelly, to enable it to transmit transverse vibrations. Again, the celebrated theory of vortices in the ether, associated with the name of Lord Kelvin, was also introduced in order to explain how the ethereal fluid could be adequately stiffened to act as an elastic vibratory fluid, capable either of mechanical or electric stress.

The difficulties surrounding this view of the ether are very numerous, however, and recent advances in electricity, especially the experimental discovery of electromagnetic waves by Hertz, and the wonderful development of their practical applications by Marconi, Lodge, Duddell, and others into wireless telegraphy and telephony, have constrained us to turn to the electromagnetic form of the undulatory theory, for a truer explanation of the beautiful form of energy which we term light, and as far more promising to elucidate finally the mystery of the ether.

The Electromagnetic Theory of Light.—A rapidly alternating condition of electric polarisation of the ether forms the fundamental assumption of this theory. The ether surrounding a body which suffers rapid alternate electrical charging and discharging, or along which a rapidly alternating electric current is passed, will naturally be polarised in two opposite senses with corresponding rapidity; and provided this change of state be regularly periodic, and occurs within the limits of rapidity corresponding to the frequency of oscillation of extreme red and violet light, the vibrations of the ether which are produced will be those which are perceived by our eyes as light. If the rapidity be less than that required for red light, the vibrations will be perceived as those of radiant heat, and if somewhat more extreme than corresponds to violet light, the radiations will be those which are so extremely active in producing chemical activity, and which we distinguish by the term ultra-violet rays; while if the rapidity be very extreme the radiations will be those which we have recently come to know as X-rays.

The attractions and repulsions exerted respectively between oppositely and similarly electrified bodies, between the opposite and similar poles of magnets, and between oppositely and similarly arranged electric circuits, can only be satisfactorily accounted for by assuming the presence of a medium which conveys the energy across the intervening space. It is equally inconceivable that the generation of an electric current in one circuit, by the starting or stoppage of a current in a neighbouring circuit, can be merely action at a distance, without the intervention of a carrying medium. It is probable that when a conducting body is electrified, or an electric current is generated in a circuit, energy is stored in the ether surrounding the conductor. This energy is used up in altering the state of the medium, which may then be said to be "polarised"; and when discharge occurs the medium is restored to its original condition. This is the essence of the theory of electricity and magnetism which is associated with the name of Clerk-Maxwell, and his view that electrical phenomena are the manifestation of the energy thus stored in the ether about a conductor is one which has as completely replaced the old fluid theory of electricity, as the undulatory theory of light has replaced the emission theory. Its bearing on the wave theory of light is of the first importance, and an adequately comprehensive idea of that theory has only been rendered possible by the remarkable practical developments already alluded to, of the use of electromagnetic ethereal waves, which have resulted in telegraphy through space.

The polarisation of the ether occurs in one of two ways, one corresponding to a positive charge of electricity and another to a negative charge. We know practically nothing at present as to the nature of this polarisation, the term being merely used to indicate a changed condition. Preston has suggested that positive and negative polarisation may be related like right- and left-handed screws or rotations, and we now know that such rotations or orbital motions do occur on the part of the electrically

charged corpuscles or electrons of which the elementary atoms are composed. But it is anyhow easy to see that if the ether surrounding a conductor can be polarised in alternate succession in the two opposite ways with adequate rapidity, a periodic disturbance or vibration will be produced, capable of generating waves of energy and propagating them throughout the ether of the surrounding space; just such waves, in fact, as we are led to consider the waves of light must be. The only conditions of this vibration of which we are yet certain are, that it is strictly periodic, and that it occurs transversely to the direction of propagation. In all probability the only other condition necessary, in order that the vibration shall give rise to those waves which affect our nerves of sight, is that it shall be sufficiently rapid, that is, that the alternation of the two opposite electric charges shall occur within the already specified limits of frequency, corresponding to red and violet light respectively.

Experimental Production of Electromagnetic Waves.—An investigation of the spark discharge of an electric condenser, such as a Leyden jar, has revealed the fact, surmised on theoretical grounds by Lord Kelvin so long ago as 1853, that the discharge is not continuous, but oscillatory. The first discharge, as it were, overreaches itself, and is followed by a recoil, the process being then repeated to and fro until equilibrium is attained. Feddersen proved the fact experimentally by means of a revolving mirror, which was caused to reflect an image of the spark into a telescope. Under suitable conditions of resistance in the circuit the image was observed to be split up into a series of bands, corresponding to separate rapidly succeeding discharges. From calculations of the time of oscillation of the discharge from a Leyden jar of ordinary size, it has been shown that such oscillatory discharges produce electromagnetic waves, varying from fifty to a hundred metres long. As the size of the jar is reduced, the wave-length correspondingly diminishes; and if we imagine the process continued until we arrive at a hypothetical condenser of the diminutive size of a chemical atom, we may expect to have waves produced corresponding in length to the extremely minute ones of light. From this it is not unreasonably deduced that the oscillating discharge of the polarised ether about the atoms or molecules (due primarily, as we shall see later, to the electrified corpuscles of which they are composed) of incandescent substances, is the actual cause of the generation of the waves of light.

The experiments of Hertz, in detecting and investigating the longer electromagnetic waves, are of incalculable importance not only to electricity but also to light, as they go far to prove the truth of the electromagnetic form of the undulatory theory of light. This form of the theory is now, in fact, the only theory of light which has stood the test of recent work; it was originally put forward from the optical point of view by MacCullagh, and subsequently from the electrical point of view, as already mentioned, quite independently by Clerk-Maxwell. Larmor has since contributed very considerably towards finally establishing the electromagnetic theory, for he has interpreted MacCullagh's results in the light of recent work, and has shown how, starting from the optical point of view, we inevitably get back to the electrical, and has thus completely bridged over the gap between MacCullagh and Clerk-Maxwell.

When a spark discharge is caused to pass between two conducting knobs, attached in each case by a wire to an electrified brass plate, one being positively and the other negatively electrified by being attached to the terminals of an induction coil, and when another circuit, consisting of a single hoop of wire supplied with knobs at the two nearly approaching ends, is brought near, it is observed that, when the length of the wire in the hoop has been properly adjusted, an induced alternating current is set up, and eventually sparks pass between the knobs at the ends of the hoop. Moreover, experiments can actually be carried out on the reflection, refraction, and interference of the electromagnetic waves produced between the two circuits; a sheet of zinc acts as an excellent reflecting screen, a parabolic sheet best of all; and a prism of pitch acts towards these electromagnetic waves as a glass prism acts towards light waves. Indeed Hertz actually measured the refractive index of pitch for the waves produced

by his apparatus. More convenient and elaborate forms of electric wave-producing and receiving apparatus have subsequently been devised by Hertz himself, Chant, Righi, and others, among which may be mentioned the magnetic detector of Rutherford and the iron filings coherer of Branley, the latter of which has proved so invaluable in the hands of Marconi and others in wireless telegraphy. Moreover, a new property of crystals has also been discovered, that of acting as a " crystal detector " for electromagnetic waves. For many crystals, in contact with a spring or plate of metal, or with another crystalline substance, are found to possess the power of " rectifying " or converting an alternating electric current into a direct one, and thus acting instead of a coherer; and they do so with the advantage that no tapping arrangement (trembler) is required (a device for disturbing the filings again out of their regular position in which the electromagnetic wave had set them and so rendering them again receptive), the crystal being always ready for further direct transmission of current. Carborundum (silicon carbide) SiC (page 688), and chalcopyrite (copper pyrites) $CuFeS_2$ (pages 200 and 698), are particularly efficacious as electromagnetic detectors, the former especially for weak currents. Several forms of apparatus have been brought to great perfection for generating electromagnetic waves of vastly increased power, so that these waves are now at the service of mankind, messages by their means speeding thousands of miles across the oceans through the ether of space—and of course with still greater facility within a smaller radius, such as that of the British Isles and their surrounding seas, or between a ship on the high seas and a distant coast, between ship and ship whether in or out of sight of each other, between an airship or aeroplane and the earth, or between two aircraft far apart on the wing—and being detected with certainty by the delicate feeling and receiving apparatus at their intended destination. The fact that they are now so thoroughly at command, and that they are essentially of the same nature as those of light, is the point which it is here desired to emphasise. Moreover, to this accomplishment of " Wireless Telegraphy " must now be added " Wireless Telephony." For the message can now be spoken verbally into a telephonic transmitter, and be received also orally by a corresponding telephonic receiver, delivering the message directly into the ear of the recipient. Moreover, a permanent record can also be obtained, the telephone message being automatically printed in plain letters on a paper tape apparatus, if it be so desired.

In all these developments the crystal detector is still very much used, and for certain purposes this remarkable property of crystals, of transmitting a current in one direction only—which has never yet been satisfactorily explained—will doubtless continue to be utilised. But in turn the crystal detector is giving place, for most purposes, to the most remarkable detector of all, the thermionic valve. Essentially this is an exhausted glass bulb or cylinder, a cross between an electric glow lamp and a Geissler vacuum tube. An electric glow lamp with carbon filament, such as was used before the coming of the metallic filament, has long been known to shoot off negative electrons when rendered incandescent by a direct current, and Edison showed that if a metal plate be also sealed into the bulb and connected to the positive terminal of the filament a small current—the thermionic current—passed. No such current was generated, however, if the plate were connected to the negative terminal. Fleming in 1904 first used this principle as a detector. The incandescent filament, of platinum, was surrounded by a cold metal (copper or nickel) cylinder. In such a case, as the potential of the cylinder increases with respect to the filament, the thermionic current increases, and finally becomes constant when all the electrons emitted from the hot wire impinge on the positively charged cylinder; the exhaustion of the bulb requires to be very high. The current passes from cylinder to filament, as negative electricity is carried by the travelling electrons from filament to cylinder and neutralises some of the positive charge on the latter. Thus the " valve " acts as a rectifier, allowing current to pass in one direction only. Moreover, it is found to

rectify high-frequency (alternating) currents as well as direct currents. Fleming's filament was heated by a battery; the aerial antenna and its transformer, condenser, and telephone (together forming the aerial receiving apparatus) were connected to the cylinder, and when electromagnetic wave-signals were received they upset the balance of the valve and current passed through the telephone, little pulses of electricity succeeding each other all in the same direction, due to the positive charges on the condenser, for the alternating negative charges of the condenser are without effect. In 1908 De Forrest discovered that it was a great advantage to introduce a third electrode, of the nature of a grid, or perforated plate, between the filament and the cylinder; and this now universal form is known as the "triode valve," in contradistinction to the earlier two-electrode form. It is with this new form that the recent marvellous advances have been made. The grid is brought as near to the plate as possible without contact. If the grid be made positive with respect to the filament (now usually of tungsten) the velocity of the electrons coming from the filament is greatly increased, but if it be made negative they are retarded, and thus the current in the valve is controlled. In actual practice the electric oscillations from the aerial source are made to alter the potential of the grid, and so the plate or cylinder current is also altered, and this produces a current in the telephone, which is placed in the plate circuit.

The triode valve is not merely a rectifier and detector, but also a remarkable amplifier of small effects (low sounds or feeble wireless signals), and can also be used as a transmitter or generator of electromagnetic waves. For by studying the "characteristic curve" of a valve the conditions can readily be attained under which a minute change in the grid potential can be made to induce a relatively immense change in the plate circuit. By using a series (cascade) of valves very remarkable amplification can be obtained. Moreover, Capt. Round has effected "tuning" by arranging that "beats" of musical value (about 500 per second) shall occur between the electromagnetic waves received and locally produced ones of the right different frequency to afford such beats, the musical note required being heard in the telephone. An efficient valve arrangement as generator is that due to W. C. White. A high anode potential requires to be used in the triode valve employed as generator, the 500-watt valve having a filament potential of 18 volts with 6 ampères, and the potential of the anode may rise to 7000 volts; in the ordinary triode valve used as amplifier and detector the filament is only at 5 volts, with a current of 0·75 ampère, and the anode is at not more than 30 volts.

Length, Distance of Propagation, and Velocity of Electromagnetic Waves.—The cylindrical oscillator employed by Chant produced waves eighty centimetres long, and with the spherical oscillator having ten-centimetre spheres he obtained electromagnetic waves 38·5 centimetres long. Righi, however, obtained waves of only 7·5 centimetres wave-length, and Lebedew obtained waves shorter than a centimetre, by using cylinders only four millimetres in length, while Baeyer has actually obtained waves only 2 millimetres long. The wave-length is determined by observations of the positions of stationary nodes, where direct and reflected waves interfere, a detector being moved along between the oscillator and a reflecting surface, until the needle of the galvanometer in the detector circuit ceases to indicate movement. The wave-length is twice the distance between two nodes. From such determinations and a knowledge of the frequency of the oscillations, the velocity of these electromagnetic waves can be calculated, and it appears to be identical with the velocity of light, 185,409 miles per second.

Polarisation of Electromagnetic Waves.—It can be proved with an oscillator and detector of any of these later forms of apparatus, mounted in parabolic reflectors, that the electromagnetic waves are plane-polarised, and that the vibrations are transverse to the line of propagation. The parabolic zinc screen reflects the waves, generated by the oscillator in the focal line of the screen, as a parallel beam towards the receiving

screen, which in turn reflects them to its focal line where the detecting apparatus is situated, precisely in the same manner as waves of light would be reflected from a pair of parabolic mirrors. The electric force is naturally parallel to the axis of the oscillator, and the magnetic lines of force being circles concentric to it, the directions of the two forces lie perpendicular to each other in the wave-front. That the oscillator acts as a polariser in producing definitely orientated vibrations will, therefore, be clearly evident, and the detector acts similarly as an analyser, for it only responds to the electromagnetic waves when the axis of its parabolic reflector is parallel to that of the oscillator. If either be rotated until its focal line is perpendicular to that of the other, sympathetic sparking ceases, exactly as, when using a pair of Nicol prisms to demonstrate the properties of polarised light, the dark field is produced when the polarising and analysing Nicols are crossed.

Moreover, one further highly interesting and significant experiment may be performed with electromagnetic waves, which not only emphasises the undoubted occurrence of polarisation, but most strikingly brings the behaviour of these waves into line with those of light, and completes the argument for their similarity. If a screen of parallel wires be placed so as to intercept the polarised electromagnetic waves proceeding from the vibrator to the synchronising receiver, it is observed that when the wires are parallel to the oscillator and to the focal lines of the parabolic reflectors the wire screen proves opaque to the waves, because it reflects them ; but when the wires are perpendicular to this direction the screen composed of them proves transparent to the waves. The former direction for opacity is parallel to the electric force, and the latter direction corresponding to transparency is parallel to the magnetic force. When, however, the oscillator and detector with their respective screens are arranged perpendicularly to each other, so that the detector is not influenced by the oscillator, and the equivalent of the dark field of the Nicols is produced, the introduction of the wire screen produces no effect when the wires are parallel to either the one or the other ; but when the wires are inclined at 45° to the axes of both oscillator and detector, the waves are transmitted and detected. For the waves are resolved into two components, vibrating respectively parallel and perpendicularly to the wires ; that component which vibrates in the former direction is naturally reflected, while the other passes to the receiver, is there again resolved into two components parallel and perpendicular respectively to the axis of the parabolic screen, and the former of these will be detected by the receiver. This result is precisely analogous to the optical one obtained when a plate of a doubly refracting crystal, cut parallel to one of the planes of optical symmetry, is introduced between crossed Nicols, first so that the two axes of the optical ellipsoid contained in that plane are respectively parallel to the two Nicols, when the dark field remains unaffected, and subsequently rotated 45° from that position, when light is transmitted, coloured when the plate is adequately thin.

Final Conclusion as to the Nature of Light.—These striking experiments, together with the fact that the velocity of electromagnetic waves is the same as that of light waves, namely, 185,400 miles or 298,500 kilometres per second—as was predicted by Maxwell would prove to be the case—and that electromagnetic waves of less than a centimetre in length have actually been experimentally produced, all concur in indicating that the waves of light and those of radiant heat only differ from these electromagnetic waves by their very much shorter wave-length. It is, therefore, practically proved that the oscillating discharge of the polarised ether about the atoms and molecules of glowing substances is the origin of the waves of light which they give forth. In the next section it will be shown that it is the moving electrified corpuscles or electrons, of which the chemical atoms are composed, that are the prime authors and originators of these electromagnetic waves of light, when the substance is heated or otherwise raised to the incandescent state ; for the radiations from the simplest of atoms, such as those of hydrogen, are not of a single wave-length, but of several different wave-lengths corresponding to the lines in the spectrum of

the element. The individual monochromatic rays, however, we shall see are due to the electrons or cycles of electrons building up the atom, so that the *tout ensemble* of all the electronic oscillations gives us the complex radiations of the atom.

The Bearing of Recent Discoveries on the further Elucidation of Light Radiation.

Beyond the unanimously accepted facts just stated very much more has lately been revealed as the result of the remarkable discoveries and investigations of cathode rays, Röntgen rays or X-rays, and of the so-called "radio-activity" of the two metals of highest atomic weight, uranium and thorium, and of the extraordinary new element next to them in order of atomic weight, radium. The terrestrial isolation of the light gaseous element helium, and the discovery of other inert gases in the atmosphere, neon, argon, krypton, and xenon, ought also to be included. For all these discoveries have a profound bearing on the nature of light and X-rays, on the constitution of the chemical atoms, and on the character of the ether itself.

Electrons or Electronic Corpuscles and X-rays.—We have in reality to go back to the discovery of the quantitative laws of electrolysis by Faraday, and his prescient views in explaining them, for the first inkling of the possibility of the existence of bodies smaller than the chemical atoms. He could only satisfactorily explain the definite relation between the electric current and the chemical work which it is able to perform by assuming the electrolyte to contain positively and negatively charged particles, the former of which go to the negative pole while the latter are delivered at the positive pole. The giving up of these electric charges at the two poles he conceived to be the cause of the production of the electric current.

After a long interval—during which the investigations of MacCullagh, Clerk-Maxwell, Lord Kelvin, Fitzgerald, and Johnstone Stoney had been consolidating the groundwork of the electromagnetic theory of light as given in the foregoing pages and as we now accept it, and the last-mentioned investigator had invented the term "electron" to signify the unit electric charge—the beautiful work of Sir William Crookes on the passage of the electric current through high *vacua* was inaugurated. One of the many results of this most fruitful investigation was to establish the fact, which was later more fully confirmed by Sir J. J. Thomson, that the rays passing from the cathode or negative terminal—generally a platinum wire fused through one end of the vacuum tube or bulb and terminating in a plate of aluminium at right angles to the wire—to the anode or positive terminal at the other end of the tube or elongated globe now currently known as a Crookes tube (illustrated in Fig. 590), when the vacuum was a very high one (the pressure of the residual gas being less than a thousandth of a millimetre of mercury), consisted of particles smaller than atoms and carrying along with them the negative charge of electricity. Johnstone Stoney's term "electron" is now currently applied to them, and it must be clearly understood that by this term (alone and unqualified) the negatively electrically charged particle is meant. Indeed, the cumulative effect of recent investigations has been to cause these electrons to be almost universally considered as actually particles

Fig. 590.—Crookes Tube, showing Shadow of Aluminium Cross interposed in Cathode Rays.

of negative electricity, although at first they were regarded as negatively electrified material particles and called corpuscles. They are produced by the disruption of the chemical atoms of the residual gas by the electric current, and are the same whatever gas has been used to fill the tube before its evacuation, although the pressure at which the disruption occurs is slightly different for different gases. They proceed in straight lines, so that if a screen, of almost any material, be placed in their path—the cross of aluminium, for instance, interposed in the pear-shaped Crookes tube shown in Fig. 590—its shadow will be thrown on the opposite positive end of the tube or bulb, the broader end of the tube shown in the illustration. When, however, they are allowed to reach the glass walls of the tube they produce brilliant phosphorescence there by their impact, lead glass giving a blue glow, soda glass a bright emerald green, and uranium glass a most brilliant green. Many crystals, such as diamonds and rubies, phosphoresce most brilliantly with characteristic colours when these cathode rays are allowed to fall on them. Fig. 591 shows a diamond belonging to Sir William Crookes phosphorescing with a bright green light in the centre of an exhausted bulb, the cathode rays being directed on it from below. South African diamonds give a bright blue phosphorescence, other diamonds many and very various tints, but often blue or greenish-blue; rubies and sapphires phosphoresce with a red colour, which in the case of the ruby is extremely brilliant.

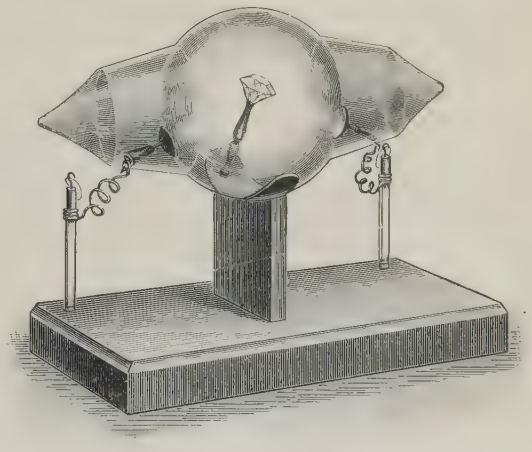

FIG. 591.—Phosphorescence of a Diamond under Impact of Cathode Rays.

The energy produced by the impact of the corpuscles or electrons is so great that if the cathode plate be made concave so as to converge the rays to a focus, even platinum when placed exactly at that focus is readily melted. Moreover, the rays are deflected when a magnet is held outside the tube, proving that they are composed of particles and are not merely an ethereal wave-motion. Perrin and Sir J. J. Thomson proved independently that negative electricity is actually transported by them.

It was subsequently discovered by Röntgen that the impact of these negatively charged corpuscles or electrons of negative electricity smaller than atoms on the walls of the Crookes tube, besides producing phosphorescence and liberating heat, gives rise to a new form of electromagnetic vibration in the ether, the now famous Röntgen or X-rays. These are akin to light-waves, merely differing in having a very much shorter wave-length and in not being a sustained wave-motion, but only a series of momentary impulses, one due to the impact of each particular particle. They owe their now extensive use in surgery to their short wave-length, which enables them to pass through the molecules of all but very dense substances. Thus glass, wood, the light metal aluminium, and incidentally flesh, are more or less pervious to them, while heavy metals like lead and, as it fortunately happens, bone, are practically impervious. They affect a photographic plate similarly to light rays, so that when the hand, for instance, is held between the excited Crookes tube and a sensitised plate in the dark, and the plate is subsequently developed, a "skiagram" or shadow photo-

graph of the bones of the hand is obtained. For the shadows of the bones are strong, leaving nearly clear glass in the negative, the X-rays being cut off by them, while those of the fleshy parts of the fingers and hand are feeble, just sufficient to indicate their outline. A gold ring on the finger gives also a strong shadow, while the crystals on it are more or less transparent. It has been shown, however, in Chapter XXXIII. on X-rays and Crystal Structure that an appreciable amount of reflection and diffraction of X-rays occurs from the planes of atoms in crystals: and that by suitably arranging the conditions most valuable information is afforded as to the nature of the crystal structure, both as regards the space-lattice formed by the grosser structural units (molecules or molecular groups) and the actual arrangement (point-system) of the atoms composing the grosser units. Indeed, a crystal acts towards the excessively minute waves of X-rays as a diffraction grating does to the relatively grosser waves of light, the only difference being that the grating is now one of three dimensions instead of being only of one dimension. For the order of the dimensions of the space-lattice cells and of the wave-lengths of X-rays is the same.

For ocular observance of the skiagrams of the parts of the human body, the photographic plate is replaced by a glass plate coated with potassium or barium

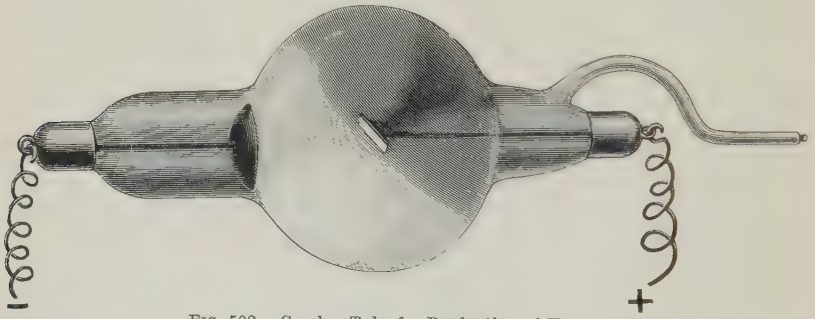

FIG. 592.—Crookes Tube for Production of X-rays.

platinocyanide, salts which fluoresce strongly when the rays impinge upon them. The main use of the rays in surgery is to locate any foreign object, a needle or bullet for instance, and also to indicate the presence of malformations, fractures, or abnormal growths of the bones themselves. The form of Crookes tube which is most suitable and efficacious for the production of X-rays is shown in Fig. 592. It is blown out of soda glass, as this is transparent to the rays, whereas lead glass is opaque to them. The negative cathode plate is of aluminium, and is concave, and the positive anode is a plate of platinum inclined at 45° to the path of the cathode rays and situated near the focus of the cathode plate, but not sufficiently exactly at the focus to cause the platinum to melt. When the tube is exhausted to a certain point the brush discharge first observed on actuating the induction coil (to which the terminals are connected by wires) becomes stratified, and the space near the concave cathode becomes dark; this dark region rapidly extends as the exhaustion approaches the desired amount, until eventually it reaches the walls of the tube, which immediately phosphoresce. Faint blue streamers, the cathode rays, may then be perceived leaving the concave aluminium cathode and converging towards the inclined platinum plate, thus moving against the direction of the current which is obviously from the positive (high potential) platinum to the negative (low potential) aluminium electrode. The negatively electrified particles or negative electrons are thus torn from the atoms present in the relatively few molecules still remaining of the gas under very low pressure in the vacuum tube, and by virtue of electrostatic repulsion they are shot off from the similarly negatively electrified cathode, with high velocity, in straight lines. Those which strike the inclined plate give rise to Röntgen X-rays. The inclined plate

then deflects these X-radiations causing the phosphorescence on to the walls of the tube on one side, and thence outside where they may be used for the purpose of producing skiagrams. This use of an inclined anode is only for convenience in getting a concentration of the Röntgen rays in one direction; any body arresting the cathode rays gives off these X-rays, and when there is no broad anode the glass walls themselves serve the purpose. In the case of the use of the inclined anode plate the Röntgen rays appear to travel in straight lines from the point where the cathode rays strike the anode.

The Röntgen rays thus appear to present to us the extreme form of ethereal wave-motion on the side of minuteness, while the electromagnetic waves employed in wireless telegraphy afford us the other extreme of long waves, and between the smallest of these latter vibrations yet experimentally produced and light-waves come the rays of radiant heat, the wave-lengths of which form a continuation of the longer waves of light belonging to the red end of the spectrum. In the same manner the extreme blue end of the visible spectrum passes into the ultra-violet chemically active rays, on the side of shortness of wave-length, after which with a considerable intervening gap we come to the extremely short wave-lengths of the Röntgen rays. It is highly interesting that the Röntgen rays are capable of producing a similar chemical action on a photographic plate to violet light-waves, showing that the gap is not so very great. The beautiful continuity of these forms of energy is one of the most striking results of these new discoveries, and it is absolutely necessary that we should follow them if we are justly to appreciate the nature and relative bearing of that form of energy, light, and also of the X-rays, with both of which the crystallographer has now so much to do, and which together reveal for him more of the internal structure of the objects of his study than probably any other agency.

Radium and Radio-activity.—As illustrating once more how one discovery leads up to another, just as the refined studies of Sir William Crookes on the electric discharge in rarefied gases led up to the discovery of the beneficent (and dangerously otherwise if not used with due precautions) X-rays by Röntgen, so experiments by Becquerel in the year 1896 as to the nature of the fluorescence which is exhibited by the substances such as potassium and barium platinocyanides, used in preparing the fluorescent screens for Röntgen-ray experiments, led to the discovery of the phenomenon now so well known as "radio-activity." For he made the unexpected observation that the salts of the heaviest of all known metals, uranium (atomic weight 236·7, that of hydrogen = 1), which are pre-eminently fluorescent, do not require to be preliminarily excited by sunlight or Röntgen waves, but that, even when freshly prepared synthetically in the dark, they have the power of emitting rays capable of passing through opaque screens and then of acting on a photographic plate. These rays were found to consist of a wave-motion of the ether, very similar to the X-rays, and, like them and violet light-waves, capable of chemical action on the sensitive layer of the plate. Now it has long been known that diamonds, certain forms of fluor-spar, wurtzite (the hexagonal form of sulphide of zinc), and the artificially prepared sulphides of zinc, barium, and calcium, glow brightly in the dark after exposure to bright sunlight, the general rule for such phosphorescence being that the phosphorescent rays are of greater wave-length than the exciting rays (see Chapter LI. for details concerning phosphorescence). But here is a substance, uranium, which of its own intrinsic nature emits rays similar to X-rays. In the year 1898 the further discovery was made independently by Schmidt and by Madame Curie—the wife of Prof. Pierre Curie of Paris, to whose work concerning the symmetry of homogeneous structures reference was made in Chapter XXX.—that this singular property was also possessed by another of the chemical elements, thorium, the next highest in order of atomic weight (230·8). But a still more surprising fact resulted from a systematic search for radio-active minerals which was then instituted by Madame Curie, namely, that the mineral from which uranium is derived, pitchblende (an impure uranoso-uranic

oxide U_3O_8), was very much more radio-active than the pure oxides of uranium which are extracted from it for the preparation of fluorescent glass. The pitchblende from the Johanngeorgenstadt mines in Austria, the richest in uranium (70 per cent.), proved to be four times as strongly radio-active as green uranium oxide U_3O_8, and three times as powerful as the black oxide U_2O_5. Moreover, the strength in radio-activity came largely from the rejected residues left after the extraction of the uranium, and after a very laborious investigation of them Madame Curie was finally rewarded by the discovery of the most wonderful of all known chemical elements, radium, which possesses the property of radio-activity *par excellence*, a million times more powerfully than uranium, and to which pitchblende very largely owes its display of the property. It was associated with the barium contained in the mineral, being the last (heaviest) member of the same Group II. (even series) to which the alkaline earth metals, calcium, strontium, and barium, belong.

Moreover, the bismuth also contained in pitchblende was found to be associated with another radio-active element, which in honour of Poland, her native country, Madame Curie named polonium. It is present in such small quantities that Marckwald, who has since discovered another mode of obtaining it from pitchblende, had to use two tons of pitchblende in order to obtain the fraction of a grain of polonium. By the end of the year 1898 these two new elements were obtained sufficiently pure to enable their spectra to be determined. In 1899 a third new element, actinium, was extracted from this important mineral, pitchblende, by Debierne, which also proved to possess radio-active properties. The atomic weights of all these five elements, uranium, thorium, radium, polonium, and actinium, are very high (see table on page 768), the three which are known with certainty being the highest of all elements. That of radium was determined by Madame Curie in the year 1908 to be 226 (225 when H = 1, 226·4 if O = 16), with a preparation of extraordinary purity, and the number has been independently confirmed in this country by Sir Edward Thorpe. We are still uncertain about the actual figures for polonium and actinium.

Metallic radium itself was actually isolated in the year 1910 by Madame Curie and A. Debierne by the electrolysis of the chloride, and found to be a brilliantly silver-white metal which melts at 700° C., altering at once in contact with air with formation of a black nitride.

Radium is constantly emitting four different things: (1) α-particles, which have been shown by Sir Ernest Rutherford, who has contributed greatly to the investigation of the radio-active elements, to consist of the positively electrically charged atoms (really the nuclei of the atoms, as presently to be explained) of the gaseous element helium (atomic weight 4), which itself had only a short time before been discovered by Sir William Ramsay to exist terrestrially, occluded in the mineral clevite, although the yellow line D_3 of its spectrum has been known for years to be characteristic of the solar chromosphere. This line had been first observed by Sir Norman Lockyer, and its wave-length carefully measured in the year 1869, and the name helium was suggested (from ἥλιος, "the sun") by his colleague Sir Edward Frankland. The α-particle, or radiant helium atom, is not quite the same thing as the ordinary atom of helium; for it is the positive nucleus with its $+2e$ charge, but without the two negative electrons $-2e$ (electrically equivalent to the $+2e$ charge of the nucleus) which together with the nucleus form the ordinary neutral atom.[1]

[1] If $-e$ be the charge carried by each negative electron, the α-particle carries a positive charge $+2e$. Thus an α-particle, with its charge $+2e$ and two negative electrons, form an electrically neutral system, and this system has been proved by Rutherford to be the normal helium atom. The positive nucleus of the helium atom, together with its charge $+2e$, is the α-particle, and its mass is practically the whole mass of the helium atom; for the mass of a negative electron is only the 1/7300th part of that of the helium atom. The size of the helium atom has been determined; its radius is almost exactly 10^{-8} cm., the one ten-millionth part of a millimetre, which is 50,000

(2) β-particles, which are negatively electrically charged corpuscles or "electrons" smaller than atoms, similar to the cathode rays of the Crookes tube. (3) γ-rays, which are of the same nature as the Röntgen X-rays. (4) An emanation of an atomic nature, which Sir William Ramsay proved in the year 1910 to be another new gaseous element of the argon series, to which he gave the name "niton" (or more probably an "isotope" of this element, as shortly to be explained), the second higher in atomic weight above xenon, its atomic weight being 222, 4 below that of radium. It appears to be intimately connected with the production of helium, which indicates that radium spontaneously decomposes into helium and niton (or its "isotope," and therefore referred to generally only as "radium emanation").

The late Sir William Crookes devised a simple arrangement which he termed a "spinthariscope" or "spark-viewer," for observing the luminous effect on a fluorescent screen, of the α-particles, the positively charged helium atoms (atomic nuclei), emitted by radium. It is shown in Fig. 593, as constructed by Messrs. R. and J. Beck. It consists of a short tube carrying a lens at one end, very much like the focussing glass used to focus the picture on the ground glass of a camera, but closed also at the other end by a screen coated with the phosphorescent sulphide of zinc (the hexagonal variety, wurtzite, usually prepared artificially by heating ordinary precipitated ZnS in a current of hydrogen), and carrying a minute speck of a salt of radium at the end of a small wire holder just in front of the centre of the screen without touching. As the charged helium atoms emitted by the radium impinge on the ZnS screen, they each render it fluorescent at the spot, and the lens resolves the spot of light into a multitude of small sparks or flashes, momentary scintillations of bright light, like a crowd of shooting-stars.

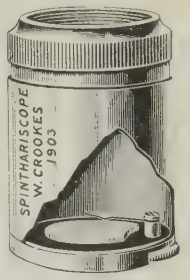

FIG. 593.—The Spinthariscope.

The explanation of these phenomena presented by radium is that the element is one so near the verge of instability, that some of its atoms (atomic weight 226·4) are constantly disintegrating, and breaking up into atoms of niton (emanation, atomic weight 222·4), α-particle helium atoms (positively charged), and β-particles, the electrons of negative electricity or electronic corpuscles negatively charged with electricity; the α-particles are (as shown on page 762) the nuclei of the ordinary atoms of helium, which emerge carrying the positive electric charge $2e$, and disrupted from their two electronic negative corpuscles, which emerge as β-particles. For, as also already shown, the ordinary atoms of helium are composed of the positive nucleus and twice as many (two) electrons as there are in the atom of hydrogen, which contains only one. The disintegration is thus essentially one into the atoms of the inert gaseous substance niton, an element of lower atomic weight, by the splitting off of helium, the latter also losing its neutral character by the tearing away of its two negative electrons, which are set free as β-particles.

It would appear that this disintegration of atoms, which occurs spontaneously with radium, is brought about in the cases of atoms of the common gases, such as hydrogen and nitrogen, by the passage of an electric current through them in the very rarefied state in which they exist in a Crookes tube. In the case of radium, the disintegration is accompanied by the liberation of heat, so much indeed as to maintain the radium salt permanently two degrees Fahrenheit higher in temperature

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times that of the negative electron (2×10^{-13} cm.). Hence the vast proportion of the spherical space enclosed by the atom is empty space. Even if another estimate of the size of the electron (2×10^{-10} cm. for its diameter) given by A. H. Compton (*Phys. Rev.*, 1919, *14*, 20), by reason of its comparability to the wave-length of the "hardest" γ-rays, be correct, the electron is still excessively smaller than the atom, and the amount of free space in the spherical system relatively enormous.

than the surrounding air. The energy previously locked up in the intra-atomic vibration of the corpuscles is thus liberated on the breaking up of the corpuscular arrangement which with the positive nucleus constitutes the atom, whatever be the nature of the arrangement, whether a series of definitely arranged cycles or any other arrangement having regular orbital or other movements about the nucleus.

Structure of the Atom.—In referring to the important work of Moseley, on p. 745 in Chapter XXXIV., it was shown that the chemical atom is now proved to be composed of a central positively charged nucleus (the relative charge on which is equal to the atomic [sequence] number N) and a number, also equal to N, of negatively electrified electronic corpuscles or electrons together electrically equal to and neutralising the positive charge on the nucleus. The number of these electrons is in general found to be about the same as the half of the number representing the atomic weight. Coming down to the simplest of the elements, those of very low atomic number, it is probable that the lithium atom (atomic weight 7 and atomic number 3) has 3 negative electrons only in its constitution, the helium atom (atomic weight 4 and atomic number 2) only 2 as just described, and finally the hydrogen atom (atomic weight and number 1) only a single β-electron. Indeed, the atomic number probably represents the exact number of the negative electronic corpuscles contained. It has been assumed that in addition to these more or less firmly held electrons of constitution, arranged about the nucleus in series of cycles as the complexity increases with the growth of the atomic number, each atom is also endowed with one, two, three, four, five, or possibly six or seven movable valency electrons, which besides controlling the chemical valency are concerned in bringing about the phenomena of conductivity. It is now probable, however, that the assumption is unnecessary, the electrons of constitution in the outer shell determining the valency and the chemical properties of the atom.

It has been very clearly put by J. H. Jeans[1] in a lecture to the Chemical Society on May 1, 1919, that the normal atom consists of a certain number, N, of negative electrons, each of charge $-e$, and a positive nucleus of extremely minute size and of charge $+Ne$, where N is the atomic number of the element. For helium $N=2$ as already shown. For hydrogen $N=1$, for lithium $N=3$, for potassium $N=19$, and so on. The negative electrons are similar, standardised, and interchangeable parts af all atoms of all elements. In the case of hydrogen, the atom (ordinary, neutral, uncharged) consists of a single negative electron of charge $-e$ and a positive nucleus of charge $+e$, the mass of which is something like 1840 times that of the negative electron. How these constituents are arranged and move inside the atom is not yet fully solved, but what has been stated in the previous few lines quoted from Jeans is probably finally and incontrovertibly settled. Both the main versions of the theory of atomic structure, those of Bohr and Sommerfeld, and of Lewis and Langmuir, presently to be described, agree on so much.

Neither the ordinary Newtonian laws of motion nor the electrostatic laws are capable of explaining the movement of the electrons in the atom, as exhibited by their spectra. The motion is discontinuous, and a formula has been discovered by Planck, involving the idea of "quanta" of energy, which does agree with the spectrum observed. For when the electron is executing isochronous vibrations the total energy of the vibration must fall into "quanta" (one, two, three, or more), and cannot involve fractions of the quantum. The "quantum" depends on the frequency of the vibration. If the frequency be v, the quantum is hv, where h is an energy constant of nature now known as "Planck's constant."[2] When an electron jumps from a vibration of n_1 quanta and frequency v_1 to another vibration of n_2 quanta and v_2 frequency, it emits instantaneously the energy $h(n_1v_1 - n_2v_2)$. Again, from photo-electric experi-

[1] *Journ. Chem. Soc.*, 1919, *115*, 865.

[2] The value of h is given as 6·53 by Langmuir, *Frank. Inst. Journ.*, 1920, *189*, 603.

ments it is found that to "ionise" an atom by light an amount of energy Q is required, and a frequency above a critical value v_0, both dependent on the nature of the atom. It is also found that $Q = hv_0$, which renders it probable that light of frequency v travels through the ether tied up, as it were, in bundles of amount hv. This is Einstein's theory of light-quanta.

On this foundation Bohr has developed his theory of line spectra and atomic structure, and it agrees wonderfully with the structure of the atom as above outlined in accordance with the work of Rutherford and of Moseley. It assumes that the negative electrons, as they grow in number with the atomic number N, build up first one ring or shell and then another, until the nucleus is surrounded by several such rings or shells by the time the heavier elements are reached, corresponding more or less to the periods of the periodic system. It accounts for Moseley's law, calculation showing that the α-lines of the K-series of X-ray spectra would arise during the passage of an electron from the second to the first ring, and the α-lines of the L-series during its passage from ring 3 to ring 2.

A slight correction is found necessary for the fact that during the movement of the electrons the nucleus is not absolutely at rest; in the case of hydrogen, for instance, it oscillates around the centre of gravity of itself and the one negative electron. A. Fowler has shown that the spectroscopic observations agree perfectly with what is to be theoretically expected when this correction is applied. Not only so, but even the fine structure of the spectrum lines is afforded when, as assumed by Sommerfeld, the orbits of the electrons are not merely regarded as circular, the simplest possible kind, but elliptical as well, which they are also capable of being. For instance, the well-known red hydrogen line C or Hα has been both qualitatively and quantitatively explained by Sommerfeld, as regards its fine structure when resolved by the high-power echelon spectroscope (see page 786 for resolution of the hydrogen lines).

When liberated from their atoms the excessively minute and light β-corpuscles or electrons move with almost incredible velocity for material particles, something like 100,000 miles per second; hence it is that they are regarded by many physicists as atoms or units of electricity. They are capable of readily passing through cloth, paper, wood, and thin sheets of metal, especially the light aluminium; indeed, the porosity to the passage of the electrons is in general inversely as the density of the material interposed. But they are stopped by non-conductors such as glass and mica, and by a dense metal sheet as thick as a penny. They are emitted not only by radium, but also by thorium and uranium, and possibly by actinium, but not by polonium. They are accompanied by the γ-rays (similar in nature to X-rays) in each case, which are much more penetrative, passing readily through an inch of solid lead or a foot of iron, and their velocity would appear to resemble that of light-waves, being nearly twice that of the β-corpuscles or electrons, which in turn is much greater than that with which the atomic α-particles of positively charged helium are emitted by radium (about 15,000 to 20,000 miles per second).

As the best source of radium is the uranium minerals, it has been suggested that radium, of atomic weight 226, is a stage (along with three helium atoms of atomic weight 4) in the disintegration of uranium, of atomic weight 238, just as niton (emanation) and helium are further stages produced by the breaking up of radium atoms. From the experimental work of Boltwood, and also according to Joly, who has studied the question from the geological point of view, there is also an intermediate substance, ionium, formed between uranium and radium. This element, however, will presently be shown to be merely another form (an isotope) of thorium. Up to and including uranium there are 92 chemical elements possible, as Moseley has definitely proved, all but 5 of which are known. One of the 5, that of atomic number 75, may be keltium, and if this should prove to be substantiated there only remain four undiscovered elements (see the accompanying periodic table, page 768).

The facts which have thus been briefly recorded enable us to carry our knowledge of the nature of matter another stage further than the atom, which for the purposes of structural crystallography we have shown in the preceding part of this book to be the unit of crystal structure, the stereometric mode of aggregation of which in a regular point-system determines the crystal class, while the molecule or small group of molecules determines, by its space-lattice mode of aggregation, the system. It was further stated, in discussing the probability of the occurrence of interspaces between the molecules and between the atoms, that the atoms themselves were probably composite, and that relatively large interspaces unoccupied by matter as we know it also occurred between the composing ultimate particles within and constituting the atom. We now perceive that the β-corpuscles or electrons and the nucleus are these ultimate particles, and that the β-corpuscles, electrons, are of paramount importance from the point of view of the nature of light vibrations, as will presently be more clearly explained. The interspaces within the atoms, however, are not readily penetrated, as the corpuscles are undoubtedly in rapid and probably organised motion within the confines, possibly restricted, which we regard as the atom or its sphere of influence. Sir W. H. Bragg has shown, however, that the α-particles (positive helium nuclei) can traverse the atoms of other elements with astonishing ease, only a few of them being deflected by collision with a nucleus, the negative electrons offering practically no resistance.

The chemical atom, the conception of which by Dalton has led directly to a century of most wonderful progress in chemistry, does not lose in importance one *iota*, as the unit of chemical constitution and of crystal structure, by this discovery of component corpuscles. On the contrary, our new knowledge of its composite nature affords us an inkling of the meaning of certain properties of atoms which have long puzzled us, and, in particular, of the meaning of their spectrum lines and of the periodicity observed in the physical and electrochemical properties of the atoms of the various elements, which is seen to occur when they are arranged in the order of their atomic weights. Why these properties are repeated in octaves, from basic (electro-positive) through neutral to acid (electro-negative), giving rise by their repetition to the family groups of similar elements which we have seen form the isomorphous series of crystalline compounds, is now no longer an enigma. This fundamental law of periodicity of the chemical elements, discovered by our countryman Newlands and termed by him the law of octaves, and worked out in numerous details by the master mind of Mendeléev,[1] is indeed clearly revealed in crystals, in the beautiful law of progression [2] of the crystal angles and structural and physical constants, according to the atomic weight of the interchangeable elements of the same family group which give rise to the isomorphous series; and its full explanation is afforded by the classical discovery of Moseley that the atomic number, which varies similarly to the atomic weight, is the fundamental constant, determining both the positive charge on the nucleus and consequently the corresponding complexity in number and cyclic arrangement of the surrounding neutralising negative β-corpuscles or "electrons." Indeed, the term "isomorphous" is now found to be only applicable to such series in the limited sense, involving this progression in regard to the crystal angles and as to every other property of the crystals, following the atomic numbers of the interchangeable elements, which has been clearly stated in previous chapters.

It is obvious that such arrangements of corpuscles can readily be imagined which

[1] See chapter iii. of the author's monograph, *Crystalline Structure and Chemical Constitution* (Macmillan & Co., 1910), for further details. To the periodic table of the elements there given the atomic weight of niton now requires to be added, 221 if H = 1 or 222·4 if O = 16, in Group VIII. Series 11, instead of the radium emanation, then thought to be 175 or 176 and to belong to Series 9. This table, with the atomic numbers added, in stronger type, and revised to February 1921, is given on page 768.

[2] A full account of the author's researches is given in the above-mentioned monograph.

shall account for this atomic periodicity, and although none of the detailed schemes yet presented may give us a fully correct picture, there can be no doubt that their principle is on right lines. Sir J. J. Thomson, for instance, has imagined the formation of the various atoms by the regular addition of cycles of these corpuscles or electrons arranged concentrically, such cycles being found to fall naturally into octaves of similar type of progression. In some such way, though possibly with other details, as imagined by Bohr and others, the electrons within the atom are supposed to be kept in regular orbital motion within its bounds, like a miniature solar system. The number of corpuscles composing the atom of the lightest of the elements, hydrogen, was at first supposed by Sir J. J. Thomson, before the discovery of the positive nucleus by Rutherford, and of the fact that practically the whole of the mass of the atom is due to it, to be as many as 800, but this number has been shown to be grossly too large, and further researches have agreed in indicating a single one as the correct number.

Indeed, it is now practically certain, as already indicated, that the atomic number N (the sequence number of the chemical element in the periodic table) not only represents the positive charge on the atom-nucleus, but also the exact number of the negatively electrified electronic corpuscles which with the positively electrified nucleus constitute the atom. The idea that there are in addition one, two, three, four, five, or possibly more up to seven valency electrons, roving corpuscles which determine the chemical-affinity property of valency, and are also concerned in electric and thermal conductivity, would appear from the most recent work to be superfluous. It is clear, however, that electric charges of negative sign are intimately associated with the β-corpuscles or electrons, and afford the explanation of their ability to produce waves of light identical in all but wave-length with experimentally produced electromagnetic waves.

According to A. H. Compton[1] the electron is a ring of "electricity" of radius $2{\cdot}5 \times 10^{-10}$ cm. Other determinations of the dimensions of the negative electron have, however, indicated the radius 2×10^{-13} cm., and this value is given by Jeans in his lecture to the Chemical Society.

The accompanying table (next page) shows the chemical elements arranged in order of atomic numbers and (in general) atomic weights, in accordance with the periodic classification.

The Atomic Number and Atomic Evolution.—It will thus be obvious that increasing importance now attaches to the atomic number[2] of an element, that is, the number which denotes the position of the element in Mendeléev's periodic table (revised up to date on the next page). As is well known, there are a few instances (argon and potassium, nickel and cobalt, iodine and tellurium) in which the place of the element is not in agreement with the atomic weight determinations; in such cases the order of the atomic numbers is followed, appropriate to the order in the table assigned by the chemical or physical properties. The values of the atomic numbers now accepted (due to Moseley) are given in stronger type. A better representation of the facts is obtained by employing a spiral in three dimensions. In this case hydrogen may be placed at the pole of the spiral. The spiral may be considered as winding down the surface of a cone, with hydrogen at the apex as the starting-point.

Thus according to the electrical theory of matter, the atom consists of a central nucleus or core, carrying a resultant positive charge, surrounded by rings (possibly co-planar) or shells of negative electrons. It was first suggested by van den Broek that the number of the place in the periodic table was the same as the number of electrons in the atom or the number of unit charges carried by the nucleus. The same suggestion was made shortly afterwards by Soddy in connection with the radio-active changes in the last thirteen places in the periodic table. The hypothesis is confirmed

[1] *Phys. Rev.*, 1918, *11*, 330; 1919, *14*, 20.

[2] An excellent memoir on the subject of Atomic Number by H. S. Allen will be found in *Journ. Chem. Soc.*, 1918, *113*, 389.

THE PERIODIC CLASSIFICATION OF THE ELEMENTS.

Series.	FAMILY GROUPS. I. R_2O.	II. R_2O_2.	III. R_2O_3.	IV. R_2O_4.	V. R_2O_5.	VI. R_2O_6.	VII. R_2O_7.	VIII. R_2O_8.
1	*1·008* **1** H = 1·000							*4·0* **2** He = 4
2	**3** Li = 6·98 *7·00*	**4** Be = 9·03 *9·1*	**5** B = 10·9 *11·0*	**6** C = 11·91 *12·00*	**7** N = 13·90 *14·01*	**8** O = 15·88 *16·00*	**9** F = 18·9 *19·0*	**10** Ne = 19·9 *20·0*
3	*23·00* **11** Na = 22·88	*24·32* **12** Mg = 24·18	*27·1* **13** Al = 26·9	*28·3* **14** Si = 28·2	*31·00* **15** P = 30·77	*32·07* **16** S = 31·82	*35·46* **17** Cl = 35·18	*39·9* **18** A = 39·6 *55·85*
4	**19** K = 38·85 *39·10*	**20** Ca = 39·7 *40·09*	**21** Sc = 44·8 *45·1*	**22** Ti = 47·7 *48·1*	**23** V = 50·8 *51·2*	**24** Cr = 51·7 *52·1*	**25** Mn = 54·6 *54·93*	**26** Fe = 55·5 **28** Ni = 58·3 *58·68* **27** Co = 58·55 (Cu = 63·1) *58·97 63·57*
5	*63·57* **29** Cu = 63·1	*65·37* **30** Zn = 64·9	*69·9* **31** Ga = 69·5	*72·5* **32** Ge = 72	*75·0* **33** As = 74·4	*79·2* **34** Se = 78·6	*79·92* **35** Br = 79·36	*82·9* **36** Kr = 82·3 *101·7*
6	**37** Rb = 84·9 *85·45*	**38** Sr = 86·94 *87·62*	**39** Yt = 88·3 *89·0*	**40** Zr = 89·9 *90·6*	**41** Cb = 92·8 *93·5*	**42** Mo = 95·3 *96·0*	**43** —	**44** Ru = 100·9 **45** Rh = 102·2 *102·9* **46** Pd = 105·7 (Ag = 107·11) *106·7 107·88*
7	*107·88* **47** Ag = 107·11	*112·40* **48** Cd = 111·6	*114·8* **49** In = 114·1	*119·0* **50** Sn = 118·1	*120·2* **51** Sb = 119·3	*127·5* **52** Te = 126·6	*126·92* **53** I = 126·01	*130·2* **54** Xe = 129·3
8	**55** Cs = 131·9 *132·81*	**56** Ba = 136·4 *137·37*	**57** La = *139·0*	**58** Ce = *140·25*	**59** Pr = *140·6*	**60** Nd = *144·3*	**61** —	
9	**62** Sa = *150·4*	**63** Eu = *152·0*	**64** Gd = *157·3*	**65** Tb = *159·2*	**66** Ho = *163·5*	**67** Ds = *162·5*	**68** Er = *167·7*	
10	**69** Tm_1 = *168·5*	**70** Tm_2 = *169·4*	**71** Yb = 170·7 *173*	**72** Lu = *174·0*	**73** Ta = 179·6 *181·0*	**74** W = 182·6 *184·0*	**75** —	*190·9* **76** Os = 189·6 **78** Pt = 193·3 *195·6* *193·1* **77** Ir = 191·5 (Au = 195·7) *197·2*
11	*197·2* **79** Au = 195·7	*200·0* **80** Hg = 198·5	*204·0* **81** Tl = 202·6	*207·10* **82** Pb = 205·35	*208·0* **83** Bi = 206·4	**84** — Polonium	**85** —	**86** Nt = 221 *222·4*
12	**87** —	**88** Ra = 225 *226·4*	**89** — Actinium	**90** Th = 230·8 *232·42*	**91** — Eka-tantalum	**92** U = 236·7 *238·5*		

The figures in heavy type are the atomic numbers, as given by Moseley.

The atomic weights in ordinary figures are those authorised by the International Committee on Atomic Weights, 1905, for hydrogen = 1, corrected and brought up to date as regards trustworthy determinations which have since been made.

The figures in italic type are on the basis of O = 16, as authorised by the International Committee.

The element ionium is isotopic with thorium, its atomic weight being 2 units less than that of thorium. Radium-D is isotopic with lead. Mesothorium-I is isotopic with radium. Mesothorium-II is isotopic with actinium. Radium-A is isotopic with polonium.

by the measurements of Barkla on the intensity of the X-radiation scattered from various substances. These indicate 7 electrons per atom of N, 8 for O, 6 for C, 16 for S, 1 for H. Rutherford's work on the scattering of α-particles by atoms of matter led him to the conclusion that the concentrated nuclear charge was approximately equal to half the atomic weight multiplied by the charge of an electron. The atomic numbers are, in fact, roughly equal to half the atomic weight.

It was, however, through the work of Moseley on the frequency of vibration of the X-rays, which are characteristic of the elements, that the importance of the atomic numbers was firmly established. The square root of the frequency of a line in the X-ray spectrum was found to be proportional to a number which increased by unity in passing from one element to the next in the periodic table. Thus every element from aluminium to gold may be characterised by an integer, N, which determines its X-ray spectrum. These atomic numbers were tabulated for the elements in question on the assumption that N for aluminium is 13. Between uranium and hydrogen only five places remain vacant.

Allen has also shown that similar considerations may be applied to chemical compounds, and that the molecular number of a compound is an additive function of the atomic numbers, that is, the molecular number N of a compound $A_a\ B_b\ C_c$ is given by the equation $N = aN_a + bN_b + cN_c$, where N_a, N_b, and N_c are the atomic numbers of the three component elements.

It may now be regarded as certain that most of the properties of the elements depend on the value of the atomic number rather than on that of the atomic weight. For example, the atomic frequency which determines the thermal behaviour of the element in the solid state has been shown by Allen [1] to bear a simple relation to the atomic number. Certain electronic frequencies are related to the atomic number in a similar way.

It will be noticed that Moseley's work does not give a unique determination of the value of N, since it is based on the assumption that N is 13 for aluminium. Rydberg has suggested that two unknown elements should be included in the periodic table between hydrogen and lithium, so that the atomic number of lithium would be 5 instead of 3. For all the elements later in the table Rydberg's ordinals would be greater than Moseley's numbers by 2 units. Evidence in favour of Moseley's numbers, however, is accumulating. Thus Barkla's results on the scattering of X-rays by air show that the number of electrons is as near to 7 for an atom of nitrogen as it is possible to estimate the pressure of the air under which the experiments were made. In the work of Allen, on the relation between atomic frequency and atomic number, it was found that the atomic numbers of Moseley gave more satisfactory agreement than did the atomic ordinals of Rydberg. The same conclusion was arrived at by van den Broek.[2]

Soddy,[3] to whom with Rutherford much credit is due for our knowledge of radioactive change, concludes that, as we pass through the successive elements in the periodic table one more negative electron is added to the outermost ring or shell for each unit increase in the positive charge N on the nucleus, or in the atomic number (which is numerically the same), and that when a certain number, 8 in the early part of the table and 18 in the later part, has been added a complete new shell or ring has become formed, which no longer participates directly in the chemical activities of the atom. Moseley has made the list of possible elements definite, and the details of the evolution (other than the above main occurrence), must, whatever they are, be such as bring about all the interesting peculiarities of the periodic classification which have been experimentally observed.

[1] H. S. Allen, *Proc. Roy. Soc.*, 1917, A, *94*, 100; *Phil. Mag.*, 1917, *34*, 478 and 488.
[2] Van den Broek, *Phil. Mag.*, 1914, *28*, 630.
[3] Lecture by Prof. F. Soddy at the Royal Institution, May 18, 1917; *Nature*, 1917, *99*, 414 and 433.

The atomic volume is undoubtedly the total volume swept out by the systems of negative electrons in orbits of revolution or in shells around the positive nucleus (which carries a single concentrated positive charge equal and opposite to that of the sum of the electrons); and beyond these rings or shells guarding the nucleus it is ordinarily impossible to penetrate. Their penetration by the very minute nuclei of helium atoms (the α-particles and next to the lightest of all positive nuclei) is quite exceptional. Chemical phenomena deal with the outermost system of electrons alone, the potentiality of loss or gain of which conditions chemical combining power. Light spectra originate in the same region, but probably the deeper systems of electrons are also involved. X-rays and γ-rays originate probably in a deep-seated ring or shell around and close to the nucleus. Mass phenomena, however, almost entirely originate in the nucleus itself. It may indeed prove to be a fact that the nucleus is identical with the "ion" of the physical chemist. The negative electrons are of mass so minute that, as already mentioned, before the nucleus was discovered by Sir E. Rutherford, it was found by Sir J. J. Thomson that a minimum of 800 would be required to make up the mass associated with the hydrogen atom; hence his first erroneous estimate of this large number of electrons in the hydrogen atom, a conclusion now known to be grotesquely wrong, as there is only one electron in the hydrogen atom, in accordance with Moseley's law, this element being No. 1 in atomic number.

Radio-active Change as Atomic Devolution with possible Production of Isotopes.—The law of radio-active change is, that the expulsion of the α-particle carrying two positive charges (the helium atom minus the two negative electrons) lowers the atomic number by 2 in accordance with Moseley's principle, and thus causes a shift of two places in the periodic table; while the expulsion of the β-particle (the negative electron) carrying a single negative charge increases the atomic number by 1 and causes a shift of one place in the opposite direction. The nucleus remains a single entity in all atoms, and practically all the mass of the atom, as just shown, is represented by it; the positive charge merely concentrates on a single nucleus with the rise in the atomic number, the mass of the nucleus correspondingly increasing as the periodic series progresses. The increase of negative electronic power, to maintain equilibrium with the growth of the positive nuclear charge, occurs by the addition of separate unit-charge-bearing electrons, one for every unit increase (the only possible mode of increase being integral, as the positive charge on the hydrogen nucleus is the smallest positive entity) in the atomic number and positive charge. When the β-particle is expelled with a sufficiently high velocity it is accompanied by γ-rays. The γ-rays are X-rays of exceedingly short wave-length, varying from 1·3 to only 0·02 Ångstrom units (an Ångstrom unit being 1×10^{-8} cm.), the shortest of this latter wave-length being the main γ-radiation from radium-C', and not resolvable by crystal gratings. The shortest wave-length resolvable by crystals is 0·072 Ångstrom units.

One very remarkable result proceeds from the above now well authenticated facts, namely, that the atomic weight is not so absolutely fixed a quantity as we have given it credit for being, and that there can be two or three different forms of the same chemical element, which have been termed "isotopes" indistinguishable both chemically and spectroscopically, but possessing atomic weights which may differ by two whole units. The first case discovered was that of niton, the last member of the argon family of inert gases; for not only is this gas produced, along with helium in the α-particle form, as the emanation in the disintegration of radium, but it is also the emanation which is afforded by both thorium and actinium. Ramsay found 222·4 for the atomic weight of niton from radium, less than that of radium (226·4) by that of helium, 4. But if in the same way we deduct two atoms of helium of total atomic weight 8 from 232·4, the atomic weight of thorium, we obtain 224·4 for the atomic weight of niton obtained from this source.

An even more interesting case is that of the element lead. It has now been proved that the radio-active elements are made up of lead and helium, for lead is their

final product, with elimination of helium at each stage of the disintegration. The uranium minerals have been shown to yield the three new radio-active elements, radium, polonium, and actinium. These three elements are, however, only intermediate members in a long sequence of changes of the parent element uranium, of atomic weight 238·5, the ninety-second and last element of Moseley's list. They are not the only radio-active elements by any means, a considerable number of others being known, each with a definite life period; but they are the only ones having a proper place each in the periodic table, and marked by distinct chemical and spectrographic properties. Three of the others are of special interest, however. One of them, radio-lead or radium-D as it has been termed, cannot be distinguished from common lead. Another, ionium, which has already been shown to be an intermediate element between uranium and radium, cannot be discriminated from thorium. And the third, called mesothorium-I, cannot be distinguished from radium. Similarly, as regards two less known radio-active elements, mesothorium-II is non-separable from actinium, and radium-A from polonium. Thallium and bismuth are also known to be identical chemically with several other still rarer radio-active elements.

Now common lead has an atomic weight of 207·1. In the disintegration of thorium of atomic weight 232·4, by the loss of six helium atoms each of atomic weight 4, a total loss of 24, we should obtain a residual element of atomic weight 208·4. Similarly, by the disintegration of uranium of atomic weight 238·5, by the loss of eight helium atoms, a total loss of 32, we should arrive at an element of atomic weight 206·5. It would thus appear that lead derived from thorium and lead derived from uranium possess atomic weights differing by about 2 units, for the mass of the liberated β-particles is too small to affect the result appreciably. Actual determinations of the atomic weight of lead from thorianite (largely ThO_2) and from pitchblende (the uranium mineral, impure U_3O_8) have been carried out, and the value for lead from the former source (using Ceylon thorite) found to be 207·8,[1] and for that from the latter source 206·1. The results have been checked and confirmed by several different workers,[2] so that it does appear to be true that lead derived during long periods of time by the disintegration of uranium has an atomic weight lower by nearly two units than that of lead obtained by the disintegration of thorium. The lead in both cases is quite indistinguishable from common lead both chemically and as regards its spectrum in light-rays and in X-rays. These two varieties of lead have been called "isotopes," that is, elements having the "same place" in the periodic table and the same atomic number (from ἴσος "equal" and τόπος "space"). The term has also now come to be applied to all such cases, such as the three nitons, and thorium and ionium. In the latter case, if we add 4 for a helium atom to the atomic weight of radium 226·4 (the change really occurring in the reverse order), we obtain 230·4 for the atomic weight of thorium, whereas the atomic weight of thorium is usually 232·4. An ordinary specimen of thorium yielded 232·1, at the same time as a determination was made in a specimen containing 30 per cent. of the ionium isotope which afforded the value 231·5. Hence, ionium would appear to have an atomic weight distinctly lower than that of thorium. Yet thorium and ionium are chemically and spectroscopically indistinguishable.

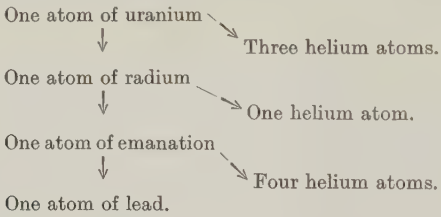
These results indicate, firstly, how much more important is the atomic number

[1] A still later result for thorium lead obtained by Honigschmid, using Norwegian thorite from Langesundfiord gave the value 207·90, the highest value yet found for lead.

[2] Richards, in his address to the American Association for the Advancement of Science, December 1918, gives further results of atomic weight determinations obtained at Harvard as follows: For ordinary lead 207·20; for pure uranium-derived lead 206·09; for radio-active lead mixed with 25 *per cent.* of ordinary lead 206·36. Honigschmid's result for pure uranium lead, 206·05, agrees remarkably well with the 206·09 Harvard result. Similar (parallel) determinations with the five metals—copper, silver, sodium, iron, and nickel—each derived from different sources, showed absolutely no difference in the atomic weight of any one of the metals.

than the atomic weight, which latter may slightly vary for the isotopic varieties when such are known; and, secondly, they clear away the great puzzle as to why there were apparently no places in the periodic table for any but three of the radio-active elements, radium, actinium and polonium, for the places are really there, namely those already occupied by the elements with which they are now shown to be isotopic.

The atoms of uranium, radium, and thorium are so big and complex as to disintegrate because of lack of stability. The disintegration in the case even of radium is slow, 1600 years being required for the decomposition of the half of any given quantity of radium, and it is incapable of being either hastened or retarded by anything man can do. Radium itself appears to have been produced by the still more exceedingly slow decomposition of uranium, the element possessing the heaviest known atoms and the highest atomic number, 92. Indeed, radium is only found in association with uranium. After a portion of uranium has been carefully purified it soon becomes again radio-active and slowly disintegrates into radium. The decomposition proceeds in a series of stages, successive atoms of helium, eight in all, being evolved with different degrees of facility, the end result being as just explained a peculiar kind of metallic lead, the isotope of ordinary lead. Lead is accordingly invariably present in radium-uranium minerals. The changes may be represented by a kind of genealogical tree as follows:



This is undoubtedly a transmutation of elements, but it is a natural and not an artificial one; transmutation of any of the chemical elements by man, in the sense understood by the alchemists, has not yet been achieved.

The similar disintegration of thorium occurs by loss of six atoms of helium, and affords the isotopic lead directly. Thus in all radio-active changes so far known there appear to be only two ultimate products, helium and lead. During the disintegration of all three of these naturally transmutable metals, uranium, radium, and thorium, radiations akin to X-rays are given forth, which in the case of radium have been already alluded to as the γ-rays. They bear away such of the colossal energy of disintegration as is not manifested as heat.

As these remarkable processes are not capable yet of being effected by human agency, a chemical element may still be defined as "a substance which has not yet been decomposed artificially," and an atom as "the smallest particle of such a substance, inferred from physico-chemical behaviour" (Prof. Theodore Richards). Dalton's laws of definite and multiple combining proportions apply without exception so long as the atoms of uranium, radium, or thorium remain intact, just as to all other elements. Indeed, the atomic theory is more securely entrenched than ever, neither Dalton's nor Avogadro's generalisations being in the least invalidated by the new facts of radio-activity. Common lead, uranium lead, and thorium lead all afford precisely the same chemical reactions, and fractional crystallisation or precipitation furnish no foreign ingredients. The atomic volumes of the elements and the refractive indices of their salts are all identical, and even couples composed of wires of common and isotopic lead afford no thermo-electric current although there is a difference of more than a unit of atomic weight between them. A slight difference in the spectra has, however, been observed, the principal line of lead derived from Australian

carnotite having been observed by Aronberg to be displaced 0·0043 Å.U. from its position as afforded by ordinary lead; the statement has been confirmed by T. R. Merton [1] for lead from thorite of Ceylon as compared with ordinary lead.

F. W. Clarke has suggested that whereas uranium and thorium lead are the result of disintegration of heavier atoms, ordinary lead may be the product of a far earlier synthesis or evolution of lead from smaller atoms. An even more probable explanation, however, is that ordinary lead of atomic weight 207 is a mixture of lead of atomic weight 206 derived from uranium with lead of atomic weight 208 derived from thorium. These two forms of lead would account for the whole of the facts now known. In the far remote ages, when all the matter now constituting the earth was liquid or gaseous, "without form and void," and undoubtedly in violent agitation, a thorough admixture of vapours would occur, including those of the isotopes of lead. The only method which offers any promise of separation of the two isotopes, when once mixed, appears to be that suggested by Richards, namely, fractional diffusion, which is concerned with the only known difference, the weight or mass of the atoms.

Uranium-Y, isotopic with Uranium-X_1 and ionium in the thorium place in the periodic table, is the first member of the actinium series. This substance uranium-Y gives a β-radiation, and its product must be the element in the ekatantalum place (atomic number 91), and be isotopic with brevium (uranium-X_2). A further α-ray change would connect ekatantalum with actinium. Now it is interesting that this new element, ekatantalum, has just been independently isolated from pitchblende by Soddy and Cranston and by Hahn and Mertner, the latter workers calling it proto-actinium. Its isotope brevium is a hopelessly short-lived substance. It is hoped that sufficient ekatantalum will be obtained to permit of confirmation of its atomic weight, and to enable its compounds to be prepared; it should, moreover, in turn, allow of the preparation of actinium in adequate quantity.

Further Details from Latest Researches concerning the Structure of Atoms.—From a careful review of the more recent work of Sir Joseph Thomson and Sir Ernest Rutherford on the nucleus, and of the latest memoirs of Bohr, Barkla, Sommerfeld, Debye, Vegard, Lewis, Langmuir, and others, it would appear that there is a general consensus of agreement on the following lines: The atomic nucleus corresponds in its positive charge to the atomic number, and as regards its mass to the atomic weight of the element. Successive elements in the periodic table are distinguished by the increment of one electron in the outermost ring or shell, until a period is completed and a new external ring or shell begins to be formed. The nuclear atom is thus a miniature solar system, the negative electrons occupying the atomic volume by their orbits, or by the shell surfaces on or about which they are in more limited motion, around the relatively excessively minute positive nucleus, wherein the mass is concentrated and which consists of or contains the integral number of positive charges expressed by the atomic number and by the number of negative surrounding electrons. The fact that the system is a very open one is proved by the observation that when an α-particle penetrates an atom, that is, enters the system, it is practically undeflected out of its path except when it passes very near to the nucleus, when it is violently swung out of its path. Thus mass and radio-activity relate to the nucleus of the atom, whereas the chemical and physical character and spectrum are determined by the planetary electrons, the chemical properties largely by the "valency" electrons in the outermost orbit or shell. The atoms of all the elements from helium to fluorine possess a first nucleus-enveloping ring or shell of two negative electrons, the exceptional atoms of the first element hydrogen having only one electron. Beginning with the next element after helium, namely lithium, a second outer ring or shell of electrons is added, consisting of from one to seven electrons as we pass along the period-series of elements from lithium up to

[1] *Nature*, 1919, *104*, 93.

fluorine, one being added for each step in atomic number, so that, with the inner ring, the total of negative electrons equals the atomic number. At neon, according to one interpretation of the results, the added electron goes to the inner (first) ring, which from now onwards possesses three electrons. The outer ring or shell of seven electrons is preserved intact as a complete second ring, from which the L-series of X-radiations originates. As the K-series of X-rays corresponding to the inner (first) ring originates by the transference of an electron from the second ring to the inner ring, it begins to be observed from sodium onwards. According to another interpretation, however, the electron added to produce neon forms the eighth of the outer ring or shell. Continuing the process, at argon a third ring or shell is completed, of eight electrons, and this ring contributes to the L-radiations (often separately distinguished as *l*-radiations), and these begin to be observed with potassium. Next, a fourth ring or shell of electrons is completed by the time nickel is reached, and this contains ten electrons (there being three elements now in Group VIII.), and this is known as the M-ring. This is followed by the formation of a fifth ring or shell of eight electrons, bringing us to krypton, and the process is then repeated from krypton to zenon, by the formation of a ten-electron ring or shell (rubidium to palladium) and an eight-electron ring or shell (silver to zenon). The next four elements, cæsium to cerium, are also produced normally, the external valency system when we arrive at cerium consisting of four electrons, corresponding to the tetradic character of that element. From now until the rare earths are completed, this external system appears to be kept intact and the new electrons added go to produce a new inner ring or shell, which is completed with the last of the rare earths, after which the new electrons are added in the normal manner.

The accompanying table is given by Vegard [1] as showing the process of evolution after hydrogen and helium in a very clear manner, by indicating the number of electrons in the outermost (surface) ring or shell. The horizontal series (periods) of elements are numbered consecutively, and these numbers in the first column indicate how many rings or shells there are in the atomic structure, including the first (innermost) ring of two or three electrons immediately next to the nucleus and the outermost or surface ring or shell in question, the number of electrons in which, indicating its degree of completeness, is given by the figures at the head of the vertical columns.

TABLE OF DISTRIBUTION OF ELECTRONS IN ATOMS.

No. of Rings in the Atom.	Number of Electrons in the Surface Ring.									
	1	2	3	4	5	6	7	8	9	10
2	Li	Be	B	C	N	O	F	Ne		
3	Na	Mg	Al	Si	P	S	Cl	Ar		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
5	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
6	Rb	Sr	Y	Zr	Nb	Mo	..	Ru	Rh	Pd
7	Ag	Cd	In	Sn	Sb	Te	I	Xe		
8	Cs	Ba	La	Ce*	Ta	W	..	Os	Ir	Pt
9	Au	Hg	Ti	Pb	Bi	Po	..	Em		
10	..	Ra	..	Th	..	U				

* At cerium there comes a rest for two whole periods covering the whole of the rare earth elements, the formation of which appears not to occur by the addition of electrons to the outer surface ring, but to the inner structure; with tantalum the ordinary procedure is resumed. This accounts for the remarkable and very similar character of the rare earths.

All through the process of evolution, according to one version of the theory, besides the structural electrons there are the external roving valency electrons, which determine the chemical and electrochemical properties of the elements, and these are

[1] *Phil. Mag.*, 1919, *37*, 238.

probably connected in some way which enables them to act together as a system. It would appear unnecessary, however, to imagine these as extra electrons, for the very fact that the outer ring or shell of electrons is capable of rising to 8 in number renders it probable that the existence of less than 8 is the cause of the valency and other chemical properties displayed by the atoms of the different elements. Thus carbon and silicon, for instance, having 4 electrons only in their outer shell, can combine with 4 others from the atoms of another element or other elements. Fluorine and chlorine having 7 electrons can each combine with one other. Neon and argon, on the other hand, having no vacancies but possessing the full possible number of 8 electrons, will have no power of chemical combination. The number of electrons in the outside ring would thus appear to be that corresponding to the " contravalency " of Abegg. It has been previously suggested that the first or second ring from the nucleus gives the K-series (probably by the passage of an electron from the second to the first ring), the second or third ring the L-series, and the third or fourth ring the M-series of X-radiations. Also, there is ground for believing that the nucleus itself is concerned with X-radiation, for a new series of very high frequency, higher than that of the K-series, have been discovered by Barkla and termed the J-series. They probably originate from the high-speed electrons within the nucleus. For there are reasons for believing that the positive charge corresponding to the atomic number is a net positive charge, and not the total, and that a small part is neutralised by negative electrons in the actual structure of the nucleus itself. The very penetrating γ-rays also arise from these nuclear electrons. Indeed, the new J-series form a link between the γ-rays of radio-active substances and the K-series of X-rays, hitherto the highest series of X-radiations known.

The characteristic X-radiations of the various elements in the periodic series and sequence are thus due to the successive rings or shells of negative electrons surrounding the positive nucleus, the wave-lengths becoming the shorter and the rays the more penetrating as the nucleus is approached. The ultra-penetrating γ-rays have been separated into three series, known as K_1, K_2, and K_3, the order being that of diminishing penetrating power, the most penetrating having the most ionising power. They may turn out to be analogous to or even identical with the three series of X-rays reflected by crystals, indeed, K_2 has already been identified with the α-line of the K-series of characteristic X-radiations of bismuth. The shortest waves yet observed are contained in the γ-rays of radium-C (see page 770). Attempts to detect still shorter rays by the crystal reflection method have not succeeded, possibly because the crystal grating is unable to resolve waves so small in comparison with the grating spaces.

It is very interesting that each ring or shell of negative electrons is not only persistent as regards the number of electrons it contains, as the more complicated elements are approached, but is also characterised by a definite quantum of energy required to dislocate it by the removal of an electron. Debye has shown that the quant-number for the ring next to the nucleus is one, for the next two rings (the L and l rings) it is two, and for the M pair of series it is three. It is now indeed definitely possible to state that each electron possesses angular momentum $m\omega r^2$ equal to $nh/2\pi$, where m is the mass of the electron, ω its angular velocity, h is Planck's constant (see page 764), r is the radius of the orbit, and n is the quant-number, an integer of ever increasing value as we pass outwards from ring to ring.

Prout's Theory revived.—Before leaving this interesting subject of the genesis or evolution of the chemical elements, reference should be made to a suggestion of W. D. Harkins,[1] made in the full light of all this recent work, that the elements are intra-atomic compounds of hydrogen, a remarkable reversion to the early theory of Prout. The suggestion is that hydrogen first becomes helium, and that this latter then acts as a secondary unit. The 91 elements other than hydrogen then fall into

[1] *Journ. Amer. Chem. Soc.*, 1917, *39*, 856; *Phys. Rev.*, 1920, *15*, 73.

two series. Those having even atomic numbers are built up of helium atoms, their general formula being nHe. Those having odd atomic numbers are built up in accordance with the general formula $n\text{He} + H_3$.

These are intra-atomic, not chemical, compounds. As regards the three atoms of hydrogen in the odd-element formula, the question arises, Are these really three separate atoms of hydrogen, or do they represent a new element of atomic weight 3? It has been suggested that the latter is correct, and that the supposed new element nebulium discovered in the nebulæ may be the element in question. This nebular substance has been subjected by interference means to an atomic weight determination by C. Fabry and H. Buisson,[1] the result being 2·7, and it is suggested that this may well really mean 3, having reference to the merely approximate nature of the method. On the other hand, however, a later atomic weight determination of the supposed nebular element nebulium by J. W. Nicholson[2] has afforded the value 1·31. The fact that so much definite evidence of the truth of Moseley's atomic numbers has now accumulated, and that those numbers leave no blank between hydrogen and helium for such a new element, renders it very unlikely, however, that nebulium is a new element at all. In this event the H_3 must refer to three atoms of hydrogen. Moreover, Aston has adduced evidence that H_3 has only one charge, and is therefore an isotope of hydrogen itself. Also Wendt and Landauer[3] have produced an active form of hydrogen which is probably H_3, by high-tension discharges in Geissler tubes at a pressure of 2 to 8 cm.

This theory of Harkins is in accordance with the manner in which radio-active elements disintegrate. The periodic system expresses the variation in the arrangement and number of the external electrons, especially the valency electrons of the outer shell, which determine the chemical and physical properties of the element; and is not concerned so much with the structure of the nucleus but only with the amount of its positive charge. The hydrogen-helium system relates, on the contrary, especially to the structure of the atomic nucleus, and this affects the relative stability and natural abundance of the elements. For if helium were formed from hydrogen in an early stage of the nebular evolution, there would be but relatively little hydrogen available as H_3. In this connection the remarkable and much discussed work of Collie may be mentioned, for it would now appear to be substantiated that he has produced small quantities of helium and neon by a powerful discharge in vacuum tubes of which the residual filling-gas was pure hydrogen. The effect is most clearly seen in the composition of meteorites, which are free from the secondary effects occurring on the earth. Now in meteorites the elements of even atomic numbers on the average are seventy times more abundant than the odd-numbered elements. The first seven elements in order of abundance are all even numbered, and make up 98·78 per cent. of the material (97·6 of stone meteorites and 99·2 of iron meteorites). The highest percentage found in meteorites of any odd-numbered element is only 1·53, and all the five yet unknown elements (either on the earth or in meteorites, those missing from Moseley's list) are odd ones. Many other facts, such as that isotopes of even-numbered elements are more numerous than those of odd-numbered ones, and that the former undergo disintegration more readily with emission of α-rays rather than β-rays, accord with this hydrogen-helium hypothesis, and predictions made on its basis have all so far been remarkably verified. The final conclusion of Harkins is that the hydrogen nucleus is the positive electron, and thus the ultimate elementary atomic unit as imagined long ago by Prout.

As an addendum to his second memoir (1920) Harkins gives the results of his

[1] *Astrophys. Journ.*, 1914, *40*, 256.
[2] *Roy. Astron. Soc. Monthly Notices*, 1918, *78*, 349.
[3] *Journ. Amer. Chem. Soc*, 1920, *42*, 930.

latest determinations of the atomic weight of chlorine, and his experimental work would appear to indicate that he has separated ordinary chlorine into two isotopes. If this be confirmed it will be the first experimental separation of an element into isotopes.

Aston and Rutherford's Remarkable Results.—Now F. W. Aston[1] in the year 1919 had devised a spectrograph which produces a spectrum (a kind of mass spectrum) for positive rays, and from the results of analyses of many of the elements conducted with it he concluded that chlorine does consist of two isotopes, of atomic weights 35 and 37. Further, that neon also is composed of two isotopes, of atomic weights 20 and 22, and that mercury consists of at least three and possibly five isotopes. In the two later memoirs (1920) he further shows that boron has two isotopes of atomic weights 10 and 11, silicon two of atomic weights 28 and 29, bromine two of 79 and 81, argon two, xenon five, and krypton no less than six isotopes (78-86). On the other hand, a considerable number of atomic weights redetermined by his method turned out to be whole integers and the elements single, comprising no isotopes, the atomic weights of carbon, nitrogen, and oxygen, for instance, being 12, 14, and 16 exactly, and those of phosphorus, sulphur, and arsenic being 31, 32, and 75 respectively. Helium and fluorine are single elements of atomic weights 4 and 19. Hydrogen is a pure element (no isotopes) of atomic weight 1·008, the only atomic weight not an integral whole number, of either a pure element or an isotope.

Prof. Eddington, in his address to Section A at the 1920 Meeting of the British Association at Cardiff, stated that Aston's results leave no doubt that all the elements are constituted of hydrogen atoms bound together with negative electrons. The nucleus of the helium atom, for instance, consists of four hydrogen atoms bound with two electrons. The atomic weight of hydrogen being 1·008 (when O = 16) and that of helium just 4, there is a loss of mass of one part in 120 occurring in the synthesis, the deficit being the electrical energy set free in the transmutation.

In his latest memoir (*Phil. Mag.*, 1920, *40*, 628), supplemented by a note in *Nature* (1920, *106*, 468) communicating the values for iodine, which proves to be a pure element, Aston gives the table on the following page, which includes all the elements which can easily be introduced, into his apparatus for obtaining mass spectra, in the form of gases or gaseous compounds. He has since given in another note in *Nature* (March 1921, *107*, 72) the results for the four alkali metals. Sodium and cæsium prove to be single (no isotopes), of atomic weights 23 and 133; while potassium and rubidium are found to be each composed of two isotopes, of atomic weights 39 and 41, and 85 and 87.

The apparatus (described *Phil. Mag.*, 1920, *39*, 611) with which these wonderfully interesting results have been achieved consists of an arrangement by which positive rays are sorted into an extremely thin ribbon by means of two parallel slits, and then spread into an electric spectrum by means of two charged plates. A portion of this spectrum, deflected through an angle θ, is selected by a diaphragm, and passed between the circular poles of a powerful electromagnet, which bends the rays back through the angle 2θ. Rays having a constant mass then converge to a focus on a photographic plate which is placed in their path, and which thus receives what may be termed a mass-spectrum. The whole arrangement is shown in the upper part *a* of Fig. 593*a*, and an enlargement of the more intricate middle portion in the lower part *b* of the figure. On the right is the discharge tube B, an ordinary X-ray bulb 20 cm. in diameter, worked by a large Ruhmkorff coil. The anode A is of aluminium rod 3 mm. thick, surrounded by an insulated aluminium tube, and the concave aluminium cathode C 2·5 cm. wide is fitted in the neck of the bulb, a small silica bulb D being placed opposite to protect the other end of the bulb from fusion by the cathode rays concentrated thereon by C. The X-ray bulb acts as its own rectifier. The details

[1] *Nature*, 1919, *104*, 393; *Phil. Mag.*, 1920, *39*, 449 and 611, and 1920, *40*, 628.

TABLE OF ELEMENTS AND ISOTOPES.

Element.	Atomic Number.	Atomic Weight.	Minimum Number of Isotopes.	Masses of Isotopes in Order of Intensity.
H	1	1·008	1	1·008
He	2	3·99	1	4
B	5	10·9	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22, (21)
Si	14	28·3	2	28, 29, (30)
P	15	31·04	1	31
S	16	32·06	1	32
Cl	17	35·46	2	35, 37, (39)
A	18	39·88	2	40, 36
As	33	74·96	1	75
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
I	53	126·92	1	127
X	54	130·2	5	129, 132, 131, 134, 136
Hg	80	200·6	(6)	(197-200), 202, 204

of the mounting of C will be clear from the lower part *b* of the figure, E being a brass collar cemented by wax, which is kept cool by a cold-water pipe of copper G. The gas to be analysed is admitted through a side tube at Q attached to the outer tube F, and a similar side tube opposite connects to the exhausting pump. The air-tight cathode C is pierced with a 3 mm. hole, coned out at the back to admit the first slit S_1. A brass plug H comes next along the brass tube, and is similarly pierced and coned and fitted with the second slit S_2. The two slits are 0·05 mm. wide by 2 mm. long, and are adjusted strictly parallel. The space between them is kept exhausted by charcoal in the side tube I_1.

The spreading of the ribbon of rays formed by the slits into an electric spectrum occurs between the two parallel flat brass surfaces J_1, J_2, 5 cm. long, held 2·8 mm. apart by glass distance-pieces; the lower surface is cut from a cylinder filling the tube, and is connected to the latter and to earth. The upper surface is that of a plate which can be raised to the desired potential by a storage battery. The plates are sloped at 1 in 20, half the angle of slope of the mean ray of the spectrum to be selected by the diaphragms K_1 and K_2, the latter of which is mounted in the bore of the stopcock L, the rotation of which enables the aperture to be varied to any desired extent, and to cut off the camera N altogether during plate-changing. After leaving the diaphragms the rays pass between the pole-pieces M of a large electro-magnet, and thence, after deflection by the magnet, to the camera N, a brass tube 6 cm. in diameter. On entering they pass between two vertical parallel plates Z, thence through a slot 2 mm. by 12 cm. cut in a cross-plate attached horizontally to the upper edges of the plates Z, to the photographic plate W, a 2 cm. strip cut length-wise from a 5 by 4 inches plate, supported above and just clear of the slot-plate. To enable this sensitive plate to be moved exactly over the rays issuing from the slot a kind of lazy-tongs gripper of the plate-carrier is provided, worked from outside by means of a torque-rod V. A small willemite (Zn_2SiO_4) screen Y is provided near the camera end, and a glass window in a cap P, for inspection purposes, closes the camera and completes the apparatus.

To photograph a mass spectrum the sensitive plate is first dried *in vacuo*, and the whole apparatus exhausted by the pump, while the stopcock L is open. The charcoal exhausters I_1 and I_2 are then cut off by stopcocks and immersed in liquid air for an hour. The electric field of 200-500 volts is then applied, and a small current sent through the magnet, sufficient to cause the bright spot due to hydrogen molecules to appear on the willemite screen Y, where it can be seen through P. Then the gas to be analysed is allowed to leak in, and the pump and induction coil are started, to get the discharge X-ray bulb into the desired state. J_1 is then earthed and the sensitive plate W moved into position over the slot. The magnet current is then finally adjusted, J_1 raised to the desired potential, and the exposure started. It may vary from 20 seconds in the case of the hydrogen lines to half an hour. The plate may then be moved sufficiently for another exposure to be made, and there is room on it for six such exposures to be made successively. The positions of the lines of the spectrum found on development are determined with the aid of a comparator and a standard

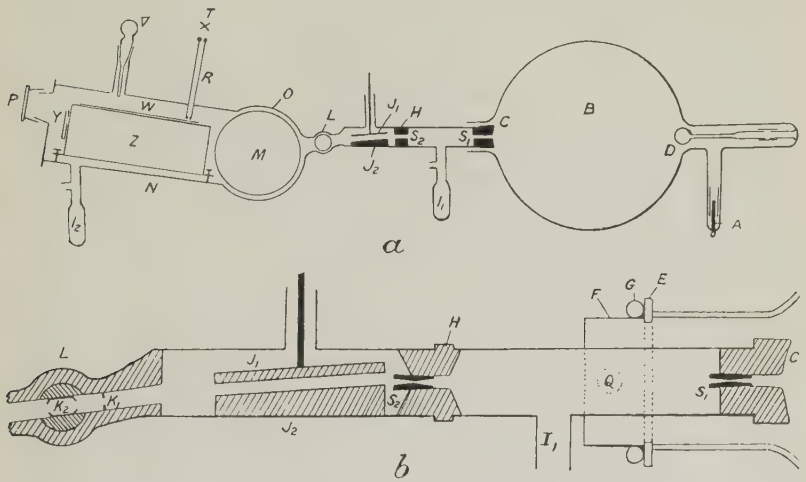


FIG. 593*a*.—Aston's Positive Ray Mass Spectrograph.

Zeiss scale. Each line is a piece of a lenticular image of the slit, and the convex edge is so very much the brightest part that it is best regarded as the line for measurement purposes. The accuracy of the position-determination is truly remarkable, being 1 in 1000.

With regard to the two isotopes of chlorine F. W. Loomis[1] has obtained evidence of the heavier isotope of atomic weight 37 in the spectrum of pure hydrogen chloride prepared from specific sources, a difference of 16 Ångstrom units having been observed for certain lines, compared with their position for ordinary hydrogen chloride, this being four times larger than the difference observed by Aronberg for the two isotopes of lead.

Sir Ernest Rutherford, in his Bakerian Lecture to the Royal Society[2] in June 1920, announced that he had actually broken down the atoms of nitrogen by bombarding them with α-particles, and that an isotope of helium of atomic weight 3 had been driven out as a result. He concluded that these helium atoms of mass 3 and carrying two units of positive electric charge are therefore constituents of the

[1] *Nature*, 1920, *106*, 180.

[2] *Proc. Roy. Soc.*, 1920, *97*, 374.

structure of the nuclei of the atoms of both oxygen and nitrogen. He had previously shown that hydrogen is a constituent of the nucleus of the nitrogen atom. Hence, the helium isotope of atomic weight 3 (which behaves like ordinary helium when it has gained two negative electrons) is probably itself composed of three hydrogen nuclei, and thus we are forced to the inevitable final conclusion that hydrogen is the ultimate constituent of all atomic nuclei. The helium isotope of atomic weight 3 is not so stable as ordinary helium of atomic weight 4, and is a constituent only of the lighter elementary atoms, while the heavier atoms, radium for instance, contain helium in the form of the isotope of atomic weight 4. The experiments of Rutherford which led to this interesting and important result are very remarkable. The α-particles were projected at high velocity through thin sheets of metal, and subsequently through both gaseous oxygen or nitrogen and solid nitride of boron. Only one α-particle in about 300,000 penetrated close to a nitrogen atomic nucleus, but when it did, owing to the very intense electric or magnetic field which occurs close to the nucleus, it was deflected off into a hyperbolic orbit which it described about the nucleus.

The Lewis-Langmuir Theory and its Explanation of Law of Atomic Diameters.—Another variety of the theory of atomic structure as regards the disposition of the negative electrons has been gradually built up by the work of Stark, Born, Landé, and especially by G. N. Lewis [1] and I. Langmuir.[2] It has been already referred to on page 715 as offering a ready explanation of the law of atomic diameters, according to which the distance between two adjacent atomic centres in a crystal structure is equal to the sum of the radii of the two atomic spheres, and which is proving so helpful in unravelling the more complicated types of crystal structure by means of the X-ray spectrometer. Instead of moving in coplanar ring or other orbits around the positively charged nucleus, as assumed in the Bohr-Sommerfeld version, the electrons are supposed to be either stationary or to rotate, revolve, or oscillate about fixed symmetrical (with a cubical tendency) positions, being distributed in three dimensions in a series of approximately spherical shells surrounding the nucleus. The successive shells, when complete, and therefore of maximum stability, contain 2 (innermost shell), 8, 8, 18, 18, and 32 (outermost shell) electrons. The chemical properties of the elements are supposed to depend on the endeavour of the elementary atom to surround itself with a more stable arrangement of electrons. An electro-positive element is one the atoms of which give up electrons in doing this, and an electro-negative element one the atoms of which take up electrons. The maximum possible stability (completion of shell) is attained in the argon family group of elements, for which the structure is as under :

Helium—a nucleus with 2 positive unit charges, surrounded by a shell containing 2 electrons.

Neon—a nucleus of charge 10, surrounded by an inner shell containing 2 electrons and an outer shell with 8 electrons.

Argon—a nucleus of charge 18, surrounded by 3 shells containing respectively 2, 8, and 8 electrons.

Krypton—a nucleus of charge 36, with 4 shells containing 2, 8, 8, and 18 electrons.

[1] *Journ. Amer. Chem. Soc.*, 1916, *38*, 762.
[2] *Ibid.*, 1919, *41*, 868 ; *Nature*, 1920, *105*, 261.

Xenon—a nucleus of charge 54, with 5 shells of 2, 8, 8, 18, and 18 electrons.

Niton—a nucleus of charge 86, with 6 shells containing respectively 2, 8, 8, 18, 18, and 32 electrons.

The elements nearest these inert gases in the periodic table revert most easily to the stable inert gas form of outer shell, especially, for instance, the alkali metals and the halogens. The underlying idea is that, as regards the elements as far as just past argon, the electrons of the outermost shell tend to form an octet, and to occupy the corners of a cube, the chemical activity of elements other than the inert gases neon and argon being due to some of the cube corners being unoccupied. In the case of helium the two electrons are supposed to lie symmetrically in a plane with the nucleus, their movement being clockwise and anti-clockwise respectively, in this plane and with equal velocities; at a certain stage, however, they are caused to retrace their paths by the repulsion of a neighbouring electron. Two distinct types of chemical combination are rendered possible. One type is exemplified in potassium chloride, a case in which the activity displayed is very great. The potassium atom, of nuclear charge and number of electrons 19, corresponding to its atomic number, is surrounded by three shells exactly as for argon of atomic number, etc., 18, together with one extra electron, the 19th. Chlorine, of atomic number, etc., 17, has the two inner shells like argon, but only 7 in the third outer one, one less than the stable arrangement. When potassium and chlorine atoms combine it is because the chlorine atom absorbs into its system the extra electron from the potassium atom. Both atoms are now surrounded by stable argon shells, but their nuclear charges of positive electricity being 19 and 17 respectively and not the corresponding 18, as in case of argon, there will be a resultant positive charge of one unit on the potassium atom and one of negative electricity on the chlorine atom. The electrostatic attraction of these charges holds the molecule together. The outer shells also exert some repulsive force on one another capable of holding the atoms apart, so as not to penetrate within the spheres to which reference has been made, and the diameters of which are those measured by the X-ray spectrometer, although the attraction would cause these spheres of the two atoms to come into contact. The nuclei, before this attraction is consummated, with their stable argon shells, may be considered as the monovalent ions (kations and anions) of potassium and chlorine respectively. Indeed, Langmuir regards the crystal of sylvine as an assemblage of potassium and chlorine ions arranged on a cubic space-lattice. In support of this part of the theory it may be mentioned that Debye and Scherrer have obtained evidence that an electron has actually passed from the lithium atom to the fluorine atom on the formation of lithium fluoride, the case being one of monovalent elements similar to that of potassium chloride just explained. Considering next an instance of polyvalent combination, say the divalent case of calcium sulphide, for example, the calcium atom loses two electrons and the sulphur atom gains two, in reverting to the

stable argon form of outer electronic shell, the resultant charges being correspondingly twice as great as in the case of potassium chloride. A noteworthy consequence of this double charge is that the increased attraction between the atoms causes all the dimensions of the structure to be reduced.

The second type of chemical combination occurs when two electro-negative elements combine. Both atoms now have fewer electrons than correspond to the stable system, and complete their outer shells with the stable number of electrons by sharing one or more electrons in common. In the cases of sulphur dioxide, SO_2, and carbon dioxide, CO_2, for instance, the atoms complete their outer shells of 8 electrons by sharing the suitable number of electrons with their neighbours.

As pointed out by A. E. Oxley,[1] this sharing of electrons often (and especially in the more complicated cases) will occur in pairs, as suggested by Langmuir, from magnetic as distinguished from electrostatic reasons; and it is to be expected that the electrons will thus be drawn into a space-pattern, characteristic for each molecule, the symmetry of which will be reflected in the crystal symmetry.

In the case of two electro-negative atoms combining, they are situated closer in the structure than electro-positive ones, because of their sharing of electrons, the spheres representing them having consequently small diameters. An electro-positive atom does not share electrons, in its outer shell, with neighbouring atoms, and is therefore further separated from other atoms and thus occupies a greater space in the structure.

In the cases of the electro-positive metals, in the free crystallised state as elementary substances, they probably consist of positive ions with inert gas shells, held together in the metallic crystal by the additional electrons, which have no fixed position, and are free to move under an electro-motive force and act as the conductors of electricity; hence the good electric conductivity of metals.

The fact that this Lewis-Langmuir version of the atomic structure theory so admirably agrees with the results of the investigations of crystal structure by X-rays renders it especially interesting and important to the crystallographer. It will be observed that the arrangement and number of the shells and of the electrons contained in them are in agreement with the table of distribution given on page 774, provided the fourth and fifth rings of the table are taken as together making up the Lewis-Langmuir fourth shell, the sixth and seventh rings their fifth shell, and the eighth and ninth rings their sixth shell. Also this version requires no additional suppositions about valency electrons, the number of electrons in the outer shell, compared with that of the complete shell of the inert gas, determining the valency in the determination of the chemical properties of the atom, as above described. The completeness with which it explains the facts, both chemical and crystallographical, is the most satisfactory feature of the theory.

The author does not regard the Bohr-Sommerfeld and Lewis-Langmuir versions of the atomic structure theory as essentially conflicting.

[1] *Nature*, 1920, *105*, 327.

It rather appears to him that as regards the parts in which they differ, while the latter version admirably expresses the facts for the ordinary and relatively low temperatures, and especially for the solid state, when electronic motion is a minimum, the former version may not be far from the truth for high temperatures and the incandescent-light-producing state. Indeed it is to be anticipated that the two versions will eventually be so correlated and combined as to afford a complete theory of the structure of matter for all attainable temperatures.

It has been essential to explain these wonderful new facts in brief form in this book on *Crystallography*, in order that the necessary material may be here available, on which to form a correct impression of the present position of the chemico-physical borderland, with which the crystallographer is ever in contact. Particularly interesting is the fact that Prout's hypothesis that all the elements are polymers of hydrogen, may now be brought up to date as an actual law, by stating that the atomic weights of all pure (without isotopes) elements, and of the separate isotopes of all those elements which are composed of two or more isotopes, are whole (integral) numbers when oxygen is taken as 16 (hydrogen being 1·008). Especially striking to the crystallographer is the beautiful manner in which Moseley's law regarding the atomic number explains the regular crystallographic progression which has been shown by the author to occur in isomorphous series, such as the rhombic sulphates and selenates, and the monoclinic double sulphates and selenates with $6H_2O$, in accordance with the progression of the atomic numbers of the interchangeable elements. For the regular increase in the mass of the atomic nucleus, as the evolution from more and more hydrogen nuclei progresses, corresponding with the rise in the atomic number, and the addition of two rings or shells (or one larger Lewis-Langmuir shell) of electrons each time, when one interchangeable element, be it the metal or the sulphur, is replaced by the next one higher (two period-series higher) in the family vertical group of the periodic table, is bound to have just the very effect in regularly modifying the morphological and optical properties of the crystals which the author has shown to occur. Why Moseley's law should so perfectly explain this crystallographic phenomenon could not have been rendered clear without giving a brief account of the facts which have now been laid before the reader.

The Zeeman Effect. — A further very remarkable phenomenon which evoked much interest when first announced was the discovery of the doubling and tripling of many of the bright lines in the spectra of the elements, under the influence of a powerful electro-magnet, the "Zeeman effect," so called in honour of its discoverer, Prof. P. Zeeman of Amsterdam. If the light radiations which correspond to the bright lines forming the spectrum of an element in the gaseous state are due to the vibrations of the atoms themselves as such, both the phenomenon of a spectrum of bright lines and that of their duplication under the agency of a magnetic field are well-nigh incomprehensible. But if the vibrations are due to the orbital or other motions of the electronic corpuscles, in rings, shells, or groups or singly according to the complexity of the atom, not only do we see why a number of lines should constitute an elementary spectrum rather than a radiation of a single wave-length, but also a most beautiful explanation is at once forthcoming for the duplication of the lines when the gas is under the influence of a magnetic field. It appears to be clear from Zeeman's researches, that a particular orbital or other motion of an electron gives rise to a specific light vibration, producing waves of a definite length, which correspond to a single bright line in the spectrum; and that the magnetic force in the Zeeman experiment affects the motion in opposite parts of the orbit in an opposite manner, in one case accelerating and in the other retarding the motion, thus producing two other bright lines owing to the slight change of frequency of the vibrations in

the two directions. These two new lines, one close on each side of the position of the original single line, and corresponding to enhanced and diminished frequencies respectively, do not necessarily entirely replace the ordinary single line when the magnet is excited. For, as Zeeman has also shown, the original line may persist, although less brilliantly; for the vibrations produced by the parts of the orbit parallel to the magnetic lines of force remain unaffected by the magnetic field. Many important contributions have been made to our knowledge of this beautiful Zeeman effect, notably by Lorentz, Larmor, Preston, Fitzgerald, and Michelson, the latter of whom has applied exquisite interference methods to its elucidation. They unite in showing that the vibrations productive of the light-waves in the ether, which give rise both to the new and to the old lines—that is, both when the vapour of the chemical element under examination is under normal conditions and when it is under the influence of the magnetic field—are the vibrations of the charged corpuscles, of the outer rings or shells of negative electrons surrounding the atomic nucleus, or the oscillatory alternation of their electric charges or of the magnetic effect which may accompany their movement; the period of any particular light-wave corresponds doubtless to the frequency of movement of the electron, or to the frequency of oscillatory electrical alternation accompanying the movement, which produces it. We may assume with Michelson that an ellipse is the most general form of the path of such a vibrating electrically charged corpuscle, and, as this can be resolved into a plane and a circular vibration, that we obtain a plane polarised and a circularly polarised ray. Again, the plane vibration may be considered as due to two oscillations in a circle, one clockwise and another anti-clockwise, and these two are oppositely affected by the magnetic field, one being accelerated and the other retarded. As the position of a spectrum line depends on the period of the light vibration which produces it, the position of the line will be altered in two opposite senses by the magnetic field when the current is passing through the electro-magnet, and doubling of the line will result. The original line persists, as already mentioned, on account of vibrations which occur parallel to the lines of force remaining unaltered. This original central line is plane polarised at right angles to the plane of polarisation of the two outer lines, which are due to vibrations in a plane perpendicular to the lines of force. This fact can be readily verified by means of a Nicol prism, either the middle line or the two outer ones extinguishing when the Nicol is at 0° and *vice versâ* when it is rotated to 90°.

Summarising in the year 1913 his researches of 1898 and 1897 in the light of more recent work Zeeman states:[1] "If a luminous gas which gives one or more sharp lines in the spectrum is immersed in a magnetic field, many of the lines are resolved into doublets or triplets, the number depending on the direction in which the light is examined. In a direction parallel to the magnetic lines of force (axial to the magnet poles) we get two, and in a direction normal to the magnetic force (equatorial) three components. The lines of the doublet are circularly polarised in opposite directions. The lines of the triplet are linearly polarised, the light of the middle line being polarised normal to the line of force and the two others in a plane parallel to the line of force. When the lines of force run towards us the right-handed circularly polarised component has the greater period." He further states that these experimental facts are quite independent of any theory, but that they agree perfectly with the theory of Lorentz, and the last fact mentioned indicates that the sign of the charge of the electrons is negative. The relation e/m, charge to mass, of the electron, worked out to be of the large order of magnitude 10^7.

Zeeman used a powerful Rühmkorff electro-magnet, and the light was analysed by a concave Rowland grating of speculum metal with a radius of curvature of 10 feet and 14,438 lines to the inch. The first spectrum was the one observed in the earlier

[1] *Researches in Magneto Optics*, Macmillan's Science Monographs, 1913.

experiments, but later also the second order spectrum was used, a micrometer eyepiece being employed ; the slit was placed near the source of light—a Bunsen flame impregnated with common salt sprinkled on asbestos—which was burning between the two magnet poles, these being only 7 mm. apart. An electromagnet with pierced poles was employed for the longitudinal effect, and the sodium lines were observed in this axial direction. Between the grating and the eyepiece were placed a quarter undulation mica plate (or a Fresnel rhomb) and a Nicol prism, in order to quench the right-handed circularly polarised light. Besides the Rowland gratings, subsequent researches showed that the Michelson interferometer (see Figs. 906 and 911) and the echelon spectroscope of Michelson (Fig. 593*b*, page 787), or a Fabry and Perot etalon (Figs. 912 and 912*a*), or a Lummer-Gehrcke parallel plate (Fig. 593*c*, page 787), may be employed to effect the resolution and analysis of the doublets and triplets. When the resolving power is not as extreme as is afforded by these beautiful methods of analysis, only a widening of the spectrum line is observed, but the alternate widening and narrowing of the line as the magnet is rapidly alternately actuated and switched off is very clearly and decisively marked, for each of the sodium lines, for instance, the observation being axial through the holes for the longitudinal effect, and equatorial for the normal effect, with the magnet turned round 90° in the horizontal plane so that the lines of force are perpendicular to the line joining the slit and the grating. In the axial position the circular polarisation of the edges of the widened sodium line is readily recognised, and in the equatorial position the plane polarisation of the edges can be plainly distinguished, the circular orbits being now seen on their edges. The change is exceedingly small, occupying a region rarely greater than 0·0000001 mm., undetected in fact by an ordinary spectroscope, a resolution being required which exhibits details a hundred times more delicate than the difference between the two sodium lines D_1 and D_2, which is only 0·0000006 mm. (6 Ångström units).[1] Using Lord Rayleigh's formula for the resolving power R of a grating, $\frac{\lambda}{\delta\lambda} = mn = R$ (where n is the total number of ruled lines and m is the order of spectrum), a spectroscope having a resolving power of 50,000 just resolves two lines separated at a distance 1-50th of that between the D lines. A resolving power of 1000 just resolves the sodium line into the doublet (D_1 and D_2). This resolving power R is not dependent on the number of lines *per* inch, but on the total number of ruled lines n constituting the grating. The normal width of the slit according to Schuster is $\frac{f\lambda}{4D}$, where λ is the wave-length, f is the focal length of the collimator objective, and D is its diameter. The normal width gives a purity of spectrum only 1·4 per cent. less than the maximum possible, but a doubling of the normal width of the slit lets in 5·7 of impurity while doubling the light (increasing it to about half the maximum possible intensity).

The largest Rowland gratings of 5 or 6 inches by 2 or 3 inches stroke, having 20,000 ruled lines to the inch, afford a resolving power of 100,000 with the first order spectrum, and this separates doublets only 1/100th of the distance apart of the two D lines. The concave gratings require no lenses, the slit, grating, and photographic plate being all the apparatus required. These fine gratings are ruled on concave

[1] An Ångström unit (written Å.U.) is 0·0000001 mm., that is, one ten-millionth of a millimetre ; it is shortly expressed as 10^{-7} mm. or, as it has recently come to be more conveniently written, in view of its direct application in this form to the dimensions of crystal structures as revealed by X-ray analysis, 10^{-8} cm. For the two sodium lines D_1 and D_2, for instance, the Ångström units are 5896 and 5890, their wave-lengths being 0·0005896 and 0·0005890 mm. A very convenient rule to remember is that 10^{-n}, when expressed as a fraction is 1 over 1 followed by n ciphers ; and when expressed in decimals is 1 in the nth decimal place after the point, preceded by $(n-1)$ ciphers in the other places. So that, for instance, 10^{-8} cm. $= \frac{1}{100,000,000}$ cm. $= 0{\cdot}00000001$ cm.

reflecting surfaces with a radius of 3 to 6 metres, the lines being equally spaced along the chord of the grating. The grating, slit, and camera are best arranged adjustably on the circumference of a circle, the radius of which is half the radius of curvature of the grating, the latter and the slit being about 120° apart. For then all the orders of spectra are sharply afforded on this same circle, and the spectrum lines of the second order occur at the position diametrically opposite to the grating and spaced proportionately to their wave-lengths.

Michelson has devised a new machine with which he has constructed a grating 9 inches long by 4½ inches stroke, having 110,000 lines in total, and with it has separated the two components of the green mercury line, which are only 1/150th of the distance of the D lines apart. But his finest achievement is the echelon spectroscope, composed of a series of 30-33 glass plates (of refractive index 1·58 for green mercury line) of perfectly equal thickness (7·8 mm.), placed in absolute (pressed) contact and stepwise arranged, each being shorter or longer than its two neighbours by a definite amount, and with it Michelson has reached a resolving power of 280,000. The light is transmitted almost normally, and whereas one part traverses a glass plate on its way the other travels through air only, and the difference in velocity gives rise to a difference of phase. For each plate the retardation is about 7800 wave-lengths. Each aperture *ab* may be considered to correspond to the line aperture of a grating. With this magnificent instrument, which is shown as constructed by Hilger in Fig. 593*b*, with a diagram below illustrating its action, Michelson discovered that many lines regarded as single are double or multiple. The red line 6438 Å.U. of cadmium, in fact, was the only line examined which proved to be truly single, although more recently the yellow line 5852 Å.U. of neon has proved equally unresolvable.[1] It reveals very clearly the doubling and tripling of the lines in the magnetic field — the Zeeman effect. Either by the echelon spectroscope or the interferometer the "visibility curves" of numerous lines of many elements have been determined, the composition of each line under ordinary circumstances, and the type of its resolution under the influence of the magnetic field, having been studied in great detail. In the meantime Zeeman, working with the second order spectrum afforded by a Rowland grating with 14,438 lines to the inch, had resolved a large number of well-known spectrum lines into triplets and doublets. The zinc line 4680 Å.U. affords an excellent example of triplet resolution (see *a* in Fig. 593*d*).

Another device for effecting high resolution, the resolving power being about 200,000, is the Lummer-Gehrcke plate, shown in Fig. 593*c*. It is a parallel plate of glass, in the form provided by Hilger 130 mm. long, 15 mm. wide, and 4½ mm. thick, the essential surfaces of which are worked very accurately plane, and are used unsilvered. The light from the source in use, say a mercury lamp, after traversing the collimator and dispersing apparatus of the spectroscope, is allowed to fall obliquely on the Lummer-Gehrcke plate, when it is internally reflected to and fro in the glass a considerable number of times, a portion of the light emerging each time. A very large difference of path is thus effected between the extremes of the various rays eventually entering the telescope of the spectroscope, and a correspondingly very high resolution thus attained, the principle being similar to that of the Michelson echelon, the Lummer-Gehrcke method effecting the object, however, with a single plate instead of a series. In order that the plate may be used as a direct vision apparatus, a small prism is cemented on one of the sides at one end, in the manner indicated in the diagram below the picture of the instrument in Fig. 593*c*; the incident

[1] T. R. Merton (*Proc. Roy. Soc.*, A, 1920, *97*, 307) has examined the red and greenish-blue lines of hydrogen, C(Hα) and F(Hβ), with an echelon grating of 35 plates each 15·085 mm. thick and with a grating step of 0·83 mm. Hα was found to be a sharp doublet, perfectly resolved, one component being twice as intense as the other; the two lines were 0·145 Å.U. apart. Hβ was only resolved when the hydrogen tube was surrounded by liquid air, and the two lines were only 0·093 Å.U. apart.

light is then reflected into the plate at a favourable angle, and the rays emerge at the other end from the other side with only a similarly slight lateral displacement. Fig. 593*c* shows the latest form of Lummer-Gehrcke plate, supported on the Hilger wave-length spectroscope (with constant deviation prism as dispersing

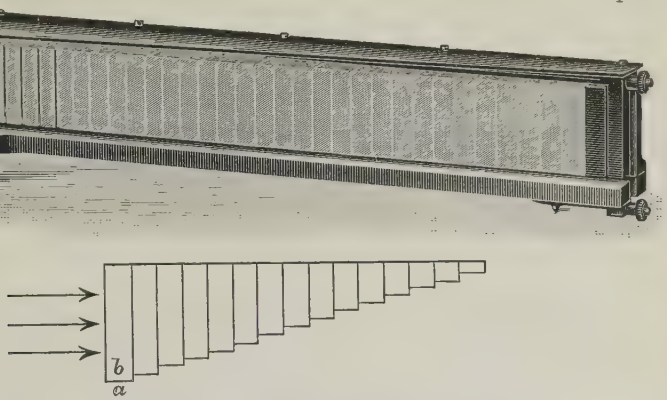


FIG. 593*b*.—The Michelson Echelon.

apparatus), in the same manner as the Fabry and Perot etalon is shown arranged in Fig. 912*a*.

The Lummer-Gehrcke plate is particularly useful for demonstrating the Zeeman effect with vacuum tubes or the mercury lamp. A small electro-magnet on an adjustable stand, with pole pieces adjustable from actual contact up to a separation of $12\frac{1}{2}$

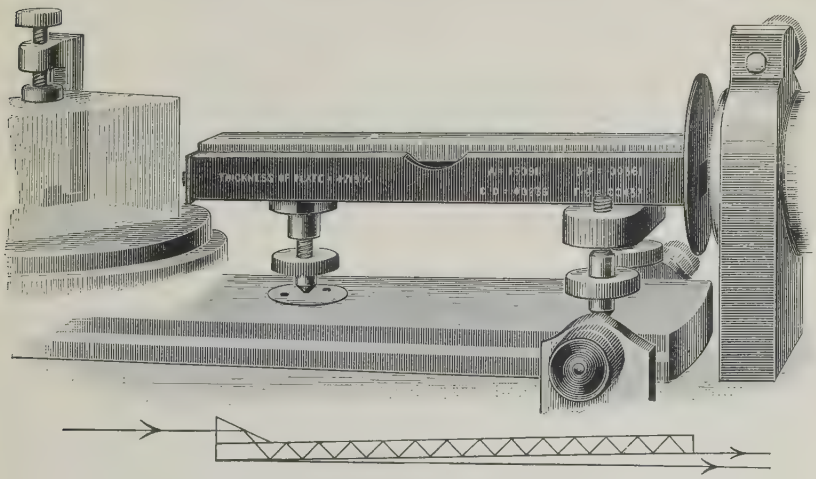


FIG. 593*c*.—The Lummer-Gehrcke Plate and Diagram of its Action.

mm., is specially provided for the purpose by Messrs. Hilger, and requires a current of only three ampères. The separation of the spectrum lines into triplets, etc., is very clearly effected. A shutter eyepiece fitted with a double image prism is also provided, by means of which the line under observation can be isolated, and the components polarised in the horizontal and vertical planes separated and observed side by side simultaneously.

Further work by Zeeman, as well as by Michelson, showed still more complex resolutions. Thus the zinc line 4722 Å.U. has been resolved into a sextet, and the green mercury line 5461 Å.U. into a nonet, nine fine lines close together at equal distances, like interference bands. Fig. 593*d* shows at *a* the resolution of the zinc line 4680 Å.U. into a triplet, at *b* that of the line 4722 Å.U. into a sextet, and at *c* that of the mercury green line 5461 Å.U. into a nonet. At *d* the figure shows the two mercury yellow lines 5770 and 5791 Å.U. resolved each into a triplet, and the rectangularly different linear polarisation of the two outside lines on the one hand and of the middle line on the other hand in each case is indicated by separating them by means of a double image calcite prism into two spectra one above the other, the vibrations in the one spectrum being horizontal and in the other vertical. The Hilger apparatus illustrated in Fig. 593*c* enables this to be achieved quite readily.

The theory of Lorentz, which not only explains these beautiful phenomena of spectral resolution into doublets, triplets, sextets, and nonets, but also to a certain

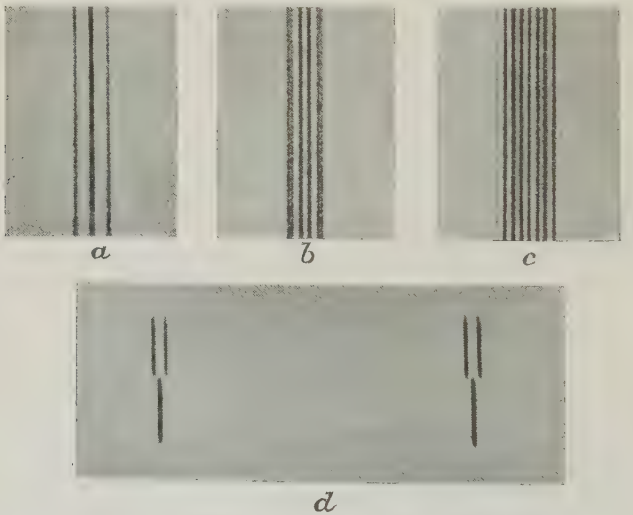


FIG. 593*d*.—Resolution of Spectrum Lines in a Magnetic Field.

extent actually predicted that they should occur, supposes that all electrical phenomena are dependent on the configuration and motion of the electrons, and that light vibrations are vibrations of the electrons. The charge, configuration, and motion of the electrons completely determine the state of the ether. When the electrons perform their motions in a magnetic field, they experience forces which cause the variation of the period and therefore the widening (as seen under a low resolving power), doubling or tripling, etc. (as seen with extreme resolving power) of the spectrum lines, and the circular or linear polarisation of the edges or of the separate lines of the little resolved group. The electrons in the atoms of a flame, in vibrating, being electrified, excite electromagnetic vibrations in the ether, constituting light when of sufficiently small period. The period of the electrons in the atoms determines the position of the lines of the spectrum, and to every variation of the period of the vibrations there corresponds a shifting of the spectrum lines. The electromagnetic force is the product evH of e the charge of the electron, its velocity v, and the magnetic force H. If the electron be charged negatively, as has been proved to be the case, the electromagnetic force is directed eastwards in the usual arrangement of the Zeeman experiment.

Now all the motions of the electrons in the atoms of a flame can be decomposed into three simple motions, just as if there were three groups of electrons vibrating in these simple ways only. One simple motion is parallel to the lines of force, and the magnetic field therefore does not affect it. The other two simple motions are circular, clockwise, or anti-clockwise, in planes normal to the lines of force. If the motion of the negative electron be right-handed the two forces are opposed and a reduction occurs, with corresponding lengthening of the period; if it be left-handed the two forces are added, and the period thereby shortened. The light caused by the circular motion is also linearly polarised when the orbits are observed sideways. Thus we get linearly polarised light with periods (times) $T - \delta T$ and $T + \delta T$, vibrating at right angles to that of the light with the period T. Hence we observe, instead of a single line, a triplet, with components polarised as already stated. This is the transverse effect. If we deal with the longitudinal effect, obtained when observing axially through the holes in the magnet poles, the light emitted being now parallel to the lines of force, the light splits up into two components $T - \delta T$ and $T + \delta T$, both of which are circularly polarised, the one right-handed and the other left-handed. Thus all the phenomena are accounted for by this theory of Lorentz. The proof that the electrons we are dealing with in light vibrations are negative and not positively charged is afforded by the facts that when the lines of force are directed towards us, and the motion of the electron is clockwise, the period of revolution is increased if the electron be negative, but decreased if positive, and that the former was what was actually observed.

Spectral Series.—A very important fact which has emerged from the spectroscopic researches of recent years, is that the spectra of many chemical elements consist of lines which are so closely connected as to belong to a series, the frequencies of all the lines of the series being capable of expression by a definite mathematical formula. It was first discovered that this was so by Balmer in the year 1885 for hydrogen, the well-known bright lines of which, the red Hα (C), greenish-blue Hβ (F), violet Hγ (near G), etc., being expressed by the formula:

$$n = N_0 \left(\frac{1}{4} - \frac{1}{m^2} \right),$$

in which n is the reciprocal of the wave-length or number of waves in a centimetre, N_0 is the number 109,675, and m represents the successive whole numbers 3, 4, 5, etc., for the three lines, etc., above respectively specified.

Balmer's formula is only valid for hydrogen, but Rydberg found another generally applicable formula for the line series of many other elements, which is:

$$n = A - \frac{N_0}{(m + \mu)^2},$$

where A is the limit of the series, N_0 is again 109,675, and μ is a constant, usually a fraction. The constant 109,675 is very remarkable, and is known as the Rydberg constant.

The different series of the same element are called the Principal Series, the Diffuse Series, and the Sharp Series; for generally there are three series, superposed, in the ordinary spectrum. The limits (limiting lines) of the diffuse and sharp series are identical, and differ from the limit of the principal series by an amount equal to the wave number (number of waves per centimetre) of the first line of the principal series.

Now it is particularly interesting, as showing how the lines of a series belong to an intimately related set or group behaving in common, that Preston discovered that for any element all the lines belonging to the same series exhibit the same resolution into triplets or doublets, etc., under the influence of the magnetic field, that is, they exhibit exactly the same Zeeman effect. Not only is the resolution for

the different lines of a series similar, but if drawn to the scale of the frequencies it is identical.

As regards the spectrum of the first element of the periodic system, hydrogen, if we take a hydrogen vacuum tube at random we shall probably find that it affords two superposed spectra, the well-known primary one (red C line, greenish-blue F line, and violet line near G), and a secondary spectrum composed of hundreds of faint lines, some of which show banded structure. Narrow tubes, such as the convenient H-shaped ones (see Fig. 890) with capillary horizontal tube connecting the two broad vertical limbs, or strong discharges, favour the primary spectrum, affording a deep red glow in the capillary; wider tubes with weaker discharges, on the other hand, exhibit best the blue glow of the secondary spectrum. Sealed tubes deteriorate rapidly, as regards the primary spectrum, owing to the evolution of gas from the electrodes, in which it had been occluded, and the addition of a large reservoir bulb consequently prolongs the life of the tube (see Fig. 720, to the right). The lines of the primary spectrum come closer together and decrease in intensity, in accordance with Balmer's formula, as we pass from red to ultra-violet; and all the lines behave in the magnetic field in the same normal way, affording triplets or doublets according as the observation is equatorial or axial with respect to the magnet poles. As regards resolution of the lines themselves under ordinary circumstances (no magnetic field) the red line C and the greenish-blue line F have been shown by Michelson and also by Merton (see footnote on page 786) to be very close doublets.

The Balmer formula for the hydrogen spectrum was subsequently derived also by Bohr from his conception of the hydrogen atom, a relatively massive but very minute nucleus positively charged, and a single electron, negatively charged, in orbital motion around it. The electron may revolve in any one of certain specified orbits known (as in astronomy) as "stationary states," and in doing so radiates no light. But when it comes under the influence of the electric discharge the electron is removed from the nucleus, and on its return it jumps from one stationary state to another, and in doing so radiates definite amounts of light energy, which determine the frequency and therefore the position of the spectrum lines. At any instant a given atom only contributes to one line; but the summation of all the radiations from a large number of atoms affords the whole series of lines of the element.

Helium affords six series, namely three (a principal, a diffuse, and a sharp series) of close doublets, including the important yellow line D_3 5876 Å.U. in the diffuse series, and also a similar three series of single lines. Now the helium atom has been shown to be a doubly positively charged nucleus, of four times the mass of the hydrogen atom, with two electrons revolving around it. Moderate discharges only detach one of the electrons, and the ordinary spectrum of helium is given when this returns to the system. Stronger discharges, however, detach both electrons but only one returns, and this is accompanied by the exhibition of a new line 4686 Å.U., first discovered in the spectrum from a single helium tube by Lockyer and Baxandall. It was thought at first to be due to some form of hydrogen, especially as it is also observed in the ring nebula in Lyra and in the star ζ Puppis. But Fowler has shown it to be entirely due to helium, of the secondary spectrum of which it forms a prominent line; to distinguish this form of helium with only one returned electron from the ordinary helium with two, it has been called proto-helium.

The spectra of many other elements have since been tackled in a similar systematic manner, and the meaning of the different series of lines has been connected with the structure of the atoms of the elements concerned. The law that the lines of the same series are similarly affected, as a whole set, by the influence of a magnetic field, has been fully substantiated throughout, and the fact that electrons are negatively, and only negatively, charged has been proved over and over again. Moreover, the beautiful work of Moseley, referred to in some detail at the close of the last chapter, as regards the high-frequency X-ray spectra, has formed a perfect continuation of

the story, and has shown that while the outer rings of electrons surrounding the nucleus of the atom are responsible for light vibrations, the more deep-seated electrons are responsible for X-radiation, and he has connected the frequencies with the structure of the atom by proving that the constant N in his formula, reminding one of Rydberg's constant N_0 in his light radiation formula, is actually the expression of the amount of the positive charge and of the actual number of electrons in the atom, as already fully described.

Summary of Conclusions as to the Nature of Light as elucidated by Recent Discoveries.—The explanation of the Zeeman phenomenon and of the spectral series would thus appear to have afforded the key to the relation of the new discoveries concerning the structure of the atom to light. At the end of the first part of this chapter we had arrived at the conclusion that the vibrations producing light waves were similar in kind, although much more minute as regards wave-length, to those producing electromagnetic waves, in the same medium, the ether, and that the vibrations were due to rapid oscillation of the electrical condition of the atoms. We have long known that the atoms of each chemical element produce a specific spectrum of bright lines when the element is in the incandescent gaseous state, and it would now appear that each line is due to some particular orbital motion in the nature of an electric oscillation, on the part of a negatively electrified corpuscle or electron or group of corpuscles or electrons, probably those chiefly which form the outer rings or shells surrounding the positively electrified nucleus of the atom. The inference is obvious, that the whole spectrum of the gas is due to the electric oscillatory impulses of the corpuscles or electrons composing the outer ramparts of the atoms and therefore that the corpuscles or electrons are concerned in and are really the authors of the vibrations of light which we attribute *en bloc* to the atoms. The real nature of the impulses we do not yet know, whether they are purely electrical or also connected with the physical movement of the negatively electrified corpuscles, or, as would appear most probable, to both combined. But we are on absolutely sure ground in concluding that the corpuscles or electrons surrounding the nuclei of the atoms are the ultimate cause of the production of light waves, and that the X-rays, of very much shorter wave-length, originate from the rings or shells of electrons nearer to the nucleus and the shortest even possibly from within the nucleus itself.

It becomes clear to us now why the vibrations of an atom do not produce light of a single wave-length, and consequently a single line in the spectrum, but rather a number of such lines. For, being a complex itself, its parts, the charged electronic corpuscles or electrons, or their groupings about the nucleus, are the authors of the separate radiations of monochromatic light, the whole being the spectrum of the atom. There is thus opened out to spectroscopy a magnificent further field for investigation, which is sure to result in supplying us with more accurate knowledge of the structure of the atom, the actual mode in which the electronic-corpuscles or electrons are arranged about the nucleus, and the nature of their orbital or more circumscribed motions. In this splendid work the co-operation of X-ray crystallographic analysis will be of the greatest value and importance, as revealing the conditions in the solid state at the ordinary temperature; and the most recent results already achieved, as described in Chapter XXXIII., would appear to indicate that fascinating and far-reaching developments are to be expected in the near future.

It is for these important reasons that it has been felt necessary, in the interests of a clear understanding of the present exceedingly interesting position, when a new world, a new state of matter, is opening before the scientific worker, to review the salient facts, which are now thoroughly established, and which cannot fail to have a profound bearing on the future both of optical and of X-ray crystallography.

CHAPTER XXXVI

LIGHT WAVES AND THEIR PROPAGATION

Characteristics of Light Waves.—The wave-motion, or wave of rapidly alternating electrical condition, with which we have to deal in the case of light, presents the following characteristics :

(1) It is energy and not matter which is propagated.

(2) Each element of ether simply oscillates, either bodily or most probably as regards its electrical condition, about its position of rest or its state of equilibrium, at right angles to the line of propagation.

(3) Through the ether of space the velocity of propagation is the same for waves of all lengths, and in all directions, namely, 185,400 miles per second.

(4) Through the ether about a material transparent substance, which is homogeneous, and either non-crystalline such as glass or crystallises in any of the forms belonging to the cubic system of symmetry, the velocity of propagation is the same in all directions, but only for waves of the same length.

(5) Through the ether about a homogeneous material transparent substance which crystallises in accordance with any of the systems of symmetry other than the cubic, the velocity not only differs for different wave-lengths, but varies with the direction according to definite laws, hereafter to be discussed, dependent on the type of symmetry.

(6) In the ether about a transparent substance which is not homogeneous, the velocity varies irregularly in different directions.

Terminology concerning Light Waves.—A graphical representation of such wave-motion is given in Fig. 594, with the important proviso that it must not be taken as implying that motion of ether particles actually occurs in the precise manner illustrated, in accordance with the older form of the undulatory theory ; but rather that such a diagram is intended to convey to the mind the idea that some change of a transverse directional character periodically occurs in the ether, probably as a rapidly alternating and oscillating change of electrical polarisation. A diagram is essential in order to explain clearly current terms regarding a wave and its parts.

In Fig. 594 a straight line of ether elements at rest is represented

by the line ABCDE of small dotted rings, and the same series in wave motion by the wavy line of solid black dots AFCGE. The wavy line AHCKE of continuous rings represents a similar wave-motion of the same particles but in an opposite phase of vibration, corresponding to total interference, extinction, and will be referred to later in this chapter. The direction of motion of the particles is in all cases transverse to the direction of propagation ABCDE of the wave, and is indicated by the dotted vertical lines. The arrows indicate the direction of motion of the particles represented by the solid black dots, along these vertical lines. Let us suppose the motion to originate at A. Each particle moves like a pendulum, with diminishing velocity, to one of the limits of its swing (indicated by the lower end L of the vertical dotted line), in a direction (that of the arrow on the vertical dotted line) transverse to the original line of particles, and after a momentary cessation of motion returns with accelerating velocity to its position of former equilibrium. It is then carried by its momentum beyond this, with again diminishing velocity, to the other limit of its swing (indicated by

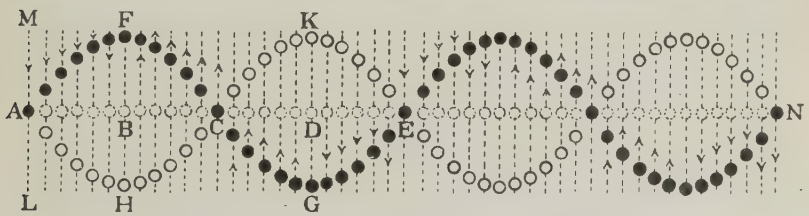


FIG. 594.—Diagrammatic Representation of Light Waves.

the upper end M of the vertical dotted line); from here it moves back again with increasing velocity to its starting-point, and thence passes on its way to make another pendulic swing. The extent of the movement LM from one limit to the other, is termed the **amplitude** of the vibration. It is proportional to the initial velocity with which the element is projected out of its position or condition of equilibrium, and consequently depends on the intensity of the energy which gives rise to the oscillation. The position of the element at any particular instant is called the **phase** of the vibration. Lastly, the time occupied in completing the vibration, that is, from the position occupied at any instant until the return of the same phase in the succeeding vibration, is termed the **period,** and its reciprocal the **frequency,** of the vibration. While this particle has been making its complete excursion, however, the motion has been communicated to the neighbouring particles, one after another, each of which has taken up the impulse to execute a similar excursion, like the swing of a pendulum, a little later than its predecessor. The result is that by the time the first particle A has actually completed its excursion, the motion has been passed along the line as far as a particle E, which will be set in motion similarly, that is, with like phase, to A, and the motion of succeeding particles will correspond to that of the succession of particles following A. Similarly, still further at like distances along

the line, there will be particles such as N vibrating with the same phase. The phase of motion thus repeats itself at regular intervals in a periodic manner. The amplitude of the vibration will naturally diminish as the energy becomes used up, and the wave-motion will eventually die out. In the case of the longer electromagnetic waves, the amplitude dies out very rapidly, hence the necessity for intense energy at the origin.

The distance between any two particles having the same phase is termed the **wave-length.** Thus AE represents diagrammatically a complete wave, as does also EN.

The relation between the wave-length λ, the velocity of propagation v, and the periodic time of the oscillations T, is expressed by the simple formula :

$$\lambda = v\mathrm{T}.$$

The periodic time T is too short to be determined directly in the case of the exceedingly rapid oscillations of light. But as the velocity and the wave-length can be determined with accuracy, the periodic time can be calculated from the equation :

$$\mathrm{T} = \lambda / v.$$

The whole wave disturbance can be represented mathematically by the equation :

$$y = a \sin \frac{2\pi}{\lambda} (vt - x),$$

in which y represents the displacement of an ether element from its position of rest in the time t, a the amplitude of the oscillations, λ the wave-length, v the velocity of propagation, and x the distance of the element from the origin.

Rectilinear Propagation of Light Waves.—The fact that light proceeds in straight lines is familiar to every one, for we invariably find an object in the direction of the rays of light which proceed from it, provided the intermediate medium is of a homogeneous character, such as the atmosphere, for instance, under ordinary conditions. Owing to the extreme minuteness of the waves of light, they appear incapable of bending round opaque objects, and consequently throw shadows of such obstacles as are placed in their way, on any background capable of reflecting the light to our eyes. This, however, is only because the amplitude of a light oscillation is so extremely small compared with the object intercepting the light ; and the phenomenon of diffraction, which we make such important use of for the purpose of producing the spectrum by means of a diffraction grating, is entirely due to the fact that when an edge is sharp enough, or a succession of such sharp edges are presented, as in the rulings of the diffraction grating (see page 822) or the very fine striations not infrequently found on crystals and discussed in Chapter XXIV., the light waves can bend round it to the precise extent which theoretical considerations based on the wave-length demand. As regards the production of ordinary shadows, however, the sharpness of such a shadow depends on the size of the source of light.

When this latter is a point, as in the case of the electric arc, the edge of the shadow will be quite sharp. But when the source of light is relatively large, such as the light from a studio window having a northerly aspect, the deep shadow or " umbra " will be bounded by a less defined " half-shadow " or " penumbra."

Intensity of Light.—The brightness or intensity of a ray of light is a function of the amplitude of the oscillation. The average energy of the vibration is proportional to the square of the amplitude. The illumination on unit surface arranged normally to the direction of the rays and at a fixed distance from the source of light is obviously proportional to the intensity of the light given forth by the source. The sum of all such units of surface is a sphere of equal illumination, the source occupying the centre and being supposed to radiate equally in all directions. If the radius of the sphere be altered, or the position (as regards distance from the source of light) of the unit portion actually used, the intensities of illumination are inversely proportional to the squares of the radii of the spheres, or to the squares of the distances of the unit screens from the source of light. This important " Law of Inverse Squares " thus determines that an equal area at twice the distance from the source of light receives only one-fourth as much illumination.

Range of Wave-length of Light Waves.—Just as the ear is only capable of perceiving as sounds vibrations in the air or other material medium which lie within certain lower and upper limits of frequency, so the eye is only capable of perceiving those oscillations in the ether which lie within two limits of frequency, corresponding to violet and red light respectively, of the wave-lengths 4×10^{-5} and 8×10^{-5} centimetre.

The rapidity with which the oscillations succeed each other in the case of violet light is thus about twice as great as what it is when red light is produced. The range of the eye is consequently a single octave, whereas every musician knows that the ear is capable of appreciating about seven octaves. But waves of greater or less frequency than those of which the eye takes cognisance are recognised in other ways. Those which are more rapid than the waves of violet light, and which constitute the " ultra-violet " light, are distinguished by their chemical activity, or actinism as it is called. They are of great importance in photography on account of the energy with which they decompose the sensitive salt (usually of silver) contained in the film of a photographic plate or sensitised paper. They probably owe this distinctive property to the fact of their shortness of wave-length, which enables them to penetrate into the molecular structure of the chemical substances which they decompose. Still shorter (even less than the one-thousandth) are the waves composing the X-rays, which are also photographically active ; the wave-length of the X-rays from a palladium anti-cathode, for instance, is given by Sir W. H. and W. L. Bragg as $0{\cdot}584 \times 10^{-8}$ centimetre. The waves somewhat longer and slower than those of the red rays announce themselves to our senses as those of heat, and the limit of these was formerly considered to be reached at a wave-length of about a four-thousandth of

a centimetre. Rubens and R. W. Wood have recently, however, isolated heat waves more than a tenth of a millimetre long, and the latest, isolated by Rubens and Baeyer, measured 0·3 mm. We have seen, however, that in wireless telegraphy we now have the means of experimenting with ether waves of lengths varying from less than a centimetre up to very great distances. As regards the waves which are visible and those which affect us as heat, there is a certain amount of overlapping; for the luminous rays also exert some heating effect, and both the non-luminous actinic and the thermal waves are converted under certain conditions, some of which were referred to in the last chapter, into luminous waves, giving rise to the phenomena of phosphorescence and calorescence. Also, the visible waves of light exert more or less actinic power, scarcely perceptible at the red end of the spectrum, but increasing rapidly as the violet end is approached.

Colour and its Dependence on Frequency of Oscillation.—Just as the number of vibrations per unit of time determines the pitch of a musical note, so the phenomenon of colour in light is due to variations in the frequency of the oscillations which give rise to luminous waves. The velocity being the same for the same medium, and the time of the oscillation varying as the wave-length, colour is also dependent under these restrictions on the wave-length. As the velocity v differs in different media, however, while the colour remains the same when light of a definite wave-length is employed at starting, and as also the frequency remains the same — that of the vibrating source — in order that the equation $\lambda = v\mathrm{T}$ may still hold (T being the reciprocal of the frequency), the wave-length must have altered proportionately to the velocity, on passing from one medium to another. Hence, speaking generally, it is the frequency of oscillation, and not the wave-length, which determines colour. It is customary, however, to associate the different colours with certain wave-lengths, but when this is done it should be understood that the original wave-length of the initial ray is meant, and, strictly speaking, its wave-length *in vacuo*.

The velocity of light of all colours *in vacuo*, that is, in ethereal space, is the same, namely, about 185,400 miles or 298,500 kilometres per second. As the wave-length is the distance through which the undulatory movement has progressed during the period of a complete oscillation, AE or EN in Fig. 594, the wave-lengths of light of the various colours must be related similarly to the corresponding periods of oscillation. The duration of oscillation is longest for red light, less and less for yellow, green, and blue respectively, and shortest for violet light, the order being that of the colours in the prismatic spectrum. The wave-length of red light *in vacuo* is about 0·000760 millimetre, and that of violet light about 0·000400 millimetre, or 4×10^{-5} cm. Consequently, in one second a ray of red light performs about 390 millions of millions (billions) of oscillations, and a violet ray about 750 billions.

The table on page 798 gives the wave-lengths of a few of the most useful spectrum lines, six of which—the three hydrogen lines, red α, greenish-blue β, and violet γ, the red lithium line, the yellow sodium

line, and the green thallium line—are those of the monochromatic rays which the author employs in all optical crystallographic measurements, such as in the determinations of refractive index and of optic axial angle. The wave-lengths of the double potassium red line α, just outside the oxygen line A of the solar spectrum, and of the two solar H and K lines due to calcium are also given as marking the approximate limits of the visible spectrum. The wave-length of the red cadmium line is included, as this is probably the most perfectly monochromatic of all the lines of the spectrum, no resolution into a double line having been observed, even with dispersions transcendently high, sufficient (with the aid of the Michelson echelon spectroscope) to resolve most other lines; this radiation is, therefore, particularly suitable for the production of interference bands for measurement purposes. The wave-lengths of the two dark red and two violet lines of rubidium, and also of the two bright blue lines of cæsium, are also included in the table, the two first because of their usefulness in marking the red beginning of the visible spectrum, even beyond the potassium line, and the two last as being very useful wave-lengths in the blue. The wave-lengths of the green and bluish-violet mercury lines are added, as the mercury vapour-lamp is now much employed in monochromatic optical work. The exceedingly prominent yellow line of the inert gaseous element neon is now also coming into considerable use, and its wave-length is, therefore, added. This radiation is as perfectly unresolvable as the red cadmium line, and is consequently of especial value in interferometry. The yellow helium line is also a useful one to work with. Both neon and helium vacuum tubes are now obtainable. These wave-lengths represent the latest and most accurate measurements.

The **Determination of the Wave-length** of a light radiation is generally achieved by means of the diffraction grating already referred to on page 794, and more fully described on page 822. The actual measurements required to be made are those of the absolute spacing d of the lines of the grating, and of the angle of diffraction θ of the ray by the grating. It will be shown on page 826 that, if n be the order of the spectrum (usually first or second), the required wave-length λ of the radiation under investigation is afforded by the equation:

$$n\lambda = d \sin \theta.$$

An even more accurate method is afforded by the use of the interferometer referred to on page 800, the experimental data required being the very accurate measurement of a standard of length, and the determination of the number of interference bands of the monochromatic radiation in question corresponding to this length. An interesting example is given in Chapter LVIII., in connection with Michelson's evaluation of the French metre in wave-lengths of light, of the determination of the wave-lengths of the red, green, and blue lines in the spectrum of incandescent cadmium vapour.

[TABLE

TABLE OF SOME PRACTICALLY USEFUL WAVE-LENGTHS.

Colour.	Spectrum Line.	Wave-length in Millimetres.	Observer.
Dark red	Rubidium	δ 0·0007950, γ 0·0007811	Kayser and Runge, 1890
„ „	Potassium α	0·0007699, 0·0007666	„ „ „
„ „	Solar A (oxygen)	0·0007594	Rowland, 1893
Deep red	Lithium α	0·0006708	Kayser and Runge, 1890
Bright red	Hydrogen α (solar C)	0·0006562	Rowland, 1893
„ „	Cadmium β	0·0006438	Michelson, 1902
Yellow	Sodium (solar D)	D_1 0·0005896, D_2 0·0005890	Rowland, 1893
„	Helium (D_3)	0·0005876	Lockyer, 1869 *
„	Neon	0·0005852	Priest, 1911
Green	Mercury	0·0005461	Kayser and Runge, 1890
„	Thallium	0·0005351	„ „ „
„	Cadmium	0·0005086	Michelson, 1902
Greenish blue	Hydrogen β (solar F)	0·0004861	Rowland, 1893
Blue	Cadmium	0·0004800	Michelson, 1902
Bright blue	Cæsium	β 0·0004593, α 0·0004555	Kayser and Runge, 1890
Bluish violet	Mercury	0·0004358	„ „ „
„ „	Hydrogen γ (near solar G)	0·0004341	Ames, 1890
„ „	Solar G (calcium)	0·0004308	Rowland, 1893
Violet	Rubidium	β 0·0004216, α 0·0004212	Kayser and Runge, 1890
„	Mercury	0·0004078, 0·0004047	„ „ „
„	Solar H (calcium)	0·0003969	Rowland, 1893
„	Solar K (calcium)	0·0003934	„ „

* Lockyer's value was 0·0005875. The mean of recent determinations (1920) is 0·0005876. The name helium was given to the substance affording this line D_3 in the sun's chromosphere by Sir Edward Frankland, who was collaborating with Sir Norman Lockyer in 1869 (*Proc. Roy. Soc.*, 1869, *17*, 350).

The waves longer than those of the extreme visible red of the spectrum are known as those of the "infra red" rays. Those shorter than the waves of the extreme visible violet are known as those of the "ultra violet" rays. Quartz and diamond are remarkably transparent to ultra violet rays, and a quartz train of lenses and prism or prisms is provided with the spectroscopes designed for the study of such waves. The refractive indices of quartz have been determined by Gifford as far as the wave-length 0·0001852 of the ultra violet rays radiated in the spectrum of aluminium. For diamond the refractive index has been determined by Miller as far as the wave-length 0·0002240 in the ultra violet.

An instrument of a spectroscopic character for the production of pure monochromatic light corresponding to any one of these wave-lengths or to any other desired wave-length, will be described in Chapter XLIV. Such an instrument is one of the first essentials for optical work with crystals.

Azimuth of Light Oscillations—Polarisation.—So far an oscillation has only been considered as occurring at right angles to the line of propagation of the wave. But it is evident that the number of perpen-

dicular directions around the line of propagation is infinite, and unless the motion of the ether element be a compound one, having a component tending to change the particular azimuth in which the oscillation starts, it is obvious that the pendulic swing will continue to recur in the same direction, and the wave produced will be composed of vibrations occurring in the same plane. A ray of light produced by such simple oscillations confined to one plane is said to be "plane polarised." It is evident that such a ray will exhibit peculiar characters in the plane containing the direction of oscillation and the line of propagation, and likewise in the rectangularly symmetrical plane containing also the latter direction and the line at right angles to this and to the direction of oscillation. Much discussion has occurred in the past as to whether the plane of polarisation is identical with the one or with the other of these two planes. The electromagnetic theory requires that something shall occur in both planes, so that both views are partly correct; the electric force concerned in the oscillations is found to be perpendicular to the plane of polarisation, and the magnetic force to be parallel to it. As some distinguishing convention is necessary, the second alternative is adopted, for reasons presently to be explained.

Crystals are particularly connected with the polarisation of light, for by far the best means of producing plane polarisation is by the use of them, their organised structure determining the polarisation of the light waves along certain of the most important structural planes. Special constraining circumstances are obviously necessary for the production of vibrations in a single plane, and these circumstances are most fortunately provided by the crystalline structure corresponding to systems of symmetry other than the cubic. Ordinary light consists of vibrations of every possible azimuth around the direction of propagation. It is supposed that the azimuth is constantly being altered by a very minute angle after every oscillation, and that a complete cycle of such changes of azimuth brings the path completely round the circle to the same again more frequently during the course of a second than the eye can discriminate, so that an ordinary ray gives the impression of being the same in all directions around the line of propagation.

Besides the rectilinear oscillations of plane-polarised light, in which the electromagnetic forces concerned occur in two fixed azimuths at right angles to each other and to the direction of propagation, others may be produced by the agency of certain crystals, in which the ether elements move in circles or ellipses.

The essential characteristic of polarised light, whether it be plane polarised, circularly polarised, or elliptically polarised, is that the directional character or orbit of the electromagnetic disturbance remains permanently the same. In the case of ordinary light, every kind of orbit and every possible variation in the directional character may possibly obtain.

Superposition and Interference of Light Waves.—Rays of ordinary light from different sources are capable of crossing each other to any extent without suffering destruction, each emerging as if the other did not exist.

The ether thus appears capable of transmitting an infinite number of different waves at the same time, and the actual condition of an ether element at any particular point must be due to the superposition of all the various disturbances which affect it, namely, the geometric resultant of the displacements which would occur if each disturbance acted singly. If we confine our attention to two rays of plane-polarised light, which have the same direction of propagation and of which the oscillations occur in parallel azimuths, but which originate from two different points in a row of ether elements, such for instance as the row ABCDE in Fig. 594, it will be clear that, in general, the two waves will differ in phase at any point which may be chosen for a study of their interference. But when the two points of origin are removed from each other by a multiple of a complete wave-length, the two wave systems will be always in the same phase, and will simply reinforce each other in brightness, the resulting wave having an amplitude equal to the sum of the amplitudes of the two component waves. When, however, the two origins are separated by half a wave-length, as in the case of the wave of solid black particles AFCGE and that of the ring-particles AHCKE in Fig. 594, or an odd multiple of this, the ether particles will be affected by the two disturbances in opposite senses, and, if the waves differ in intensity, the resultant wave-movement will have the phase of the stronger of the two, and an amplitude equal to the difference of the amplitudes of the two individual rays. In the special case shown in Fig. 594 where two such waves are of equal intensity, they will destroy each other completely, the light being extinguished.

We shall make very considerable use of this phenomenon of "interference" in our optical study of crystals, in distinguishing between isotropic, uniaxial, and biaxial crystals, also in connection with the measurement of the angle between the optic axes of biaxial crystals, and with the determination of the sign of double refraction by means of a quartz wedge. The principle will also be employed in the dilatometer for the determination of the thermal expansion of crystals, the interferometer, which is used in connection with the dilatometer, being the most delicate measuring apparatus yet invented, the unit of the scale of interference bands being half a wave-length of red hydrogen (or cadmium) light, one three-thousandth of a millimetre or one seventy-seven thousandth of an inch; as the interval between two such interference bands (dark straight bands parallel to each other on a brilliantly illuminated red ground, as seen through the interferometer telescope) can be divided by the eyepiece micrometer into a hundred parts, we are actually able to measure with this instrument to the extraordinary degree of fineness of the eight-millionth part of an inch or the three-hundred thousandth of a millimetre. The thousandth of a millimetre is the finest measurement possible by the most refined mechanical means, including the use of the most delicate micrometer. Moreover, so absolutely infallible is the recurrence of a dark band at every half wave-length, where the nodes of light-extinction occur, and so exactly alike are the wave-lengths themselves when the light

employed is strictly monochromatic (such as that corresponding to the red spectrum line of cadmium), that no mistake is possible. The two rays which are thus caused to interfere are reflected from two absolutely plane glass surfaces, which are inclined at a very minute angle to each other but to the eye are apparently parallel; one of them is fixed in space while the other moves with the expanding crystal, or with whatever other movable object is under investigation and the movement of which is to be measured. The amount of motion is obtained at once by multiplying the number of bands and any final fraction of a band which have moved past the centre of reference (a little silver ring in the centre of one of the two glass surfaces, and which is focussed in the centre of the field of the observing telescope) by the half-wave-length of the light employed, usually red cadmium or red hydrogen light. The instrument itself is described in Chapter LVII., and a further application of it to the determination of the elastic bending and twisting of plates and bars of crystals in Chapter LVIII.

If two waves originate from points removed by other distances than the wave-length or an odd multiple of half a wave-length, the resultant wave will possess both different phase and different amplitude. Hence two such waves as we have been considering can, according to the separation of the points of origin, vary in their resultant from the sum of the two intensities down to zero, the plane of the vibrations remaining the same.

When the planes of polarisation are different, while the direction of propagation remains the same, the resultant wave will be either circularly or elliptically polarised. The resultant is a circularly polarised wave when the amplitudes are the same, the planes of polarisation at right angles, and the difference of phase one quarter of a wave-length. The case is analogous to that of a pendulum, which is started vibrating in one plane, and to which, when at one extremity of its path, one quarter of a complete swing from the original position of rest, an impulse of equal strength is imparted at right angles to the first impulse, which results in a circular motion being described by the bob of the pendulum (see Fig. 666, page 909). The period of oscillation of such circularly polarised light is the same as that of the two component oscillations. We shall employ a "quarter-wave plate" of mica in our practical optical work with crystals, for producing a circularly polarised beam of light, which affords characteristic phenomena with crystals of different symmetry.

If the amplitude of the oscillations of the two component rays be different, or if the difference of phase be other than one quarter of the wave-length, or again, if the inclination of the two planes of polarisation be other than 90°, the resultant movement of the ether elements takes the form of an ellipse, and the resultant ray is elliptically polarised.

Propagation of Light—Wave Surface.—The consideration of single waves and simple cases of superposition just concluded lead naturally to the discussion of the whole series of waves emanating in all directions from the oscillating source. The nature of the whole disturbance is

dependent primarily on the constitution of the medium in which it is propagated, for it is this which determines whether the waves are transmitted in the different directions with the same or with different velocity. The ether of space, that is *in vacuo*, where ponderable matter as we yet know it—molecules, atoms, nuclei, and electronic-corpuscles—is excluded, is a medium of the first kind, transmitting the light waves in all directions with equal velocity. Likewise the ether surrounding the molecules of transparent gases and liquids, and also the ether which penetrates between the molecules of such transparent solids as are constituted exactly alike in all directions, behaves as a medium of the first kind. Such an optically homogeneous substance is glass, and such also are all crystalline transparent solids which crystallise according to the cubic system of symmetry, the essence of which is perfect symmetry in all three rectangular directions of space, the physical properties being, as we have seen (page 583), represented by a sphere. The term "isotropic" is used to distinguish such homogeneous media. Through them light of any one particular colour is transmitted with equal velocity in every direction. The ether penetrating these isotropic substances is, indeed, only distinguished from that of vacuous space by the fact that light of different colours does not traverse them with equal velocity, the specific velocity for any particular colour being a characteristic of the particular substance. It is obvious why gases and liquids should be isotropic, for their molecules being in a state of motion, free and rapid in the case of gases but of a rolling character in liquids, it is an average effect which is produced on light, there being no congelation into an organised and rigid solid structure in which the molecules have definite homogeneously distributed positions, as in the case of a crystal. Glass would appear to owe its isotropic character to the great viscosity of the substance in the molten state at temperatures not far removed from the melting point, which causes it to retain on solidification the infinitely heterogeneous positions of the molecules which obtained in the liquid state just before solidification, the great viscosity at this point preventing the organised crystallographic arrangement of the molecules of the silicate or silicates present. That this is a correct view is proved by the formation of crystallites in some glasses by slow devitrification, such as those in the pitchstone of the Isle of Arran shown in Fig. 17 on page 29. The reason for the isotropy of cubic crystals is one of quite an opposite nature, namely, the most perfect development of organised crystallographic arrangement, that of the cubic system of symmetry with three equal and rectangular crystallographic axes, with its inevitable accompaniment when the symmetry is fully developed, the display of the maximum possible number of planes and axes of symmetry.[1]

The continuous *locus* of points just about to be disturbed in an

[1] Although the crystals of all the five classes (Nos. 28 to 32) of the cubic system are isotropic, a few substances of class 28, such as sodium chlorate and bromate, sodium sulphantimoniate, and sodium uranyl acetate, rotate the plane of polarisation of light, by virtue of the enantiomorphism of their crystal structure and their possession of screw axes without any planes of symmetry.

isotropic medium, under the influence of a light oscillation of definite frequency, will evidently be a spherical surface. For instance, at the moment of the completion of a vibration of the oscillating source, the surface connecting all the ethereal elements to which the complete wave has travelled will be a sphere of radius λ, the wave-length. At the end of a second vibration the disturbance will have reached the surface of a sphere of radius 2λ, and so on. Such a sphere of like phase is termed a wave-surface or wave-front, and the term may be extended to any surface joining ether elements in a like phase of vibration, of which those spheres having radii which are multiples of the wave-length are only special cases.

Every point on a wave-surface may be regarded as a new centre of disturbance, and the secondary waves travelling out from it may be considered as carrying on the wave-motion. The envelope of these secondary waves will be identical with the wave-front of the main dis-

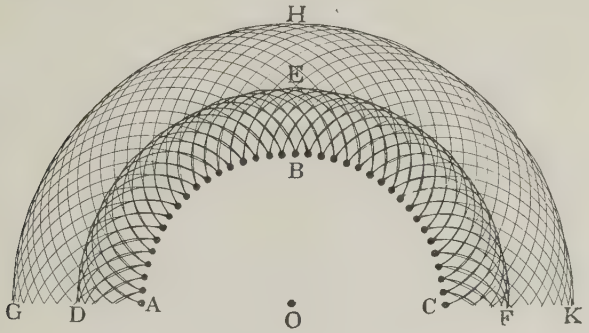


FIG. 595.

turbance, so that the aggregate effect of the secondary waves is the primary wave. The construction of radiating wave-motion as a succession of wave envelopes is the well-known principle of Huyghens. It will be rendered clearer by Fig. 595, which embodies the so-called Huyghens construction. If, instead of considering the motion as really originating at O, we consider a circular line of particles ABC on the spherical wave-front at any moment, each of these particles may be considered as an origin, and if we draw a circle from each, having a radius corresponding to the distance the movement has travelled from the particle in a given further time t, we shall arrive at the circular section DEF by drawing the enveloping curve of all such circles. Similarly, if the time considered be $2t$, and we draw a further series of circles from the points on the circle ABC with radius corresponding to $2t$ we arrive at the circular section of the outer envelope GHK. Obviously these spherical envelopes DEF and GHK are identical with the primary spherical wave-surfaces for the same moments of time.

In the case of the simple homogeneous media now under consideration, for which it has been shown that the envelope or wave-front is a

spherical surface, the individual rays will obviously be the normals to the wave-front; that is to say, the wave moves out from the oscillating centre of disturbance along the radii of its spherical front, and at right angles to the tangent to the wave-front at the point where the particular radius considered meets the wave-front. Thus, for isotropic media in general, the direction of propagation of the wave is always at right angles to the wave-front.

The more complicated cases of the passage of light through anisotropic media, that is, through crystals belonging to the systems of symmetry other than the cubic system, will be discussed in later chapters. It will be obvious that the wave-surface in these cases cannot be spherical, and it will be shown that, in general, it is an ellipsoid. Also the wave-front is not, in general, perpendicular to the direction of propagation, although it is so when the direction is one of the three principal axes of the ellipsoid.

We have thus seen that the consideration of the nature of light, and of the mode of propagation of its electromagnetic waves, leads us inevitably and naturally to the investigation of the optical properties of crystals. The two subjects of optics and crystallography are as intimately, and indeed indissolubly, bound up together as is the latter subject with chemistry and mineralogy. It has been considered both right, therefore, and advisable, inasmuch as recent investigation has so enormously widened our conception of the nature of light and of the true character of the chemical atom, that the real study of the optical properties of crystals, to which we shall now proceed, should have been preceded by these two introductory chapters, which have thus naturally paved the way for our practical studies in optical crystallography.

CHAPTER XXXVII

THE FUNDAMENTAL OPTICAL CONSTANT, INDEX OF REFRACTION; AND ITS RELATIONS TO THE ANGLES OF TOTAL REFLECTION AND OF POLARISATION—DIFFRACTION AND THE GRATING

BEFORE we can with advantage pass to the consideration of the optical ellipsoid expressive of the optical properties of crystals, and its bearing on practical crystallography, it is imperative that we should be quite clear as to the elementary facts concerning the passage of light through transparent media, and the nature of the all-important constant, refractive index. For on this knowledge depends our means of practically determining that constant. Before considering crystal-media, however, we will assume that our transparent medium is non-crystalline, glass for instance; or at any rate if crystalline that it possesses the symmetry and internal structure of the cubic system, so that it is singly refractive, or "isotropic," the optical properties being the same in all directions within the substance. We must first investigate what happens when a beam of light traverses a transparent plate or a prism of such a substance, determine the conditions for partial and total reflection at either of its surfaces, and deduce a general means of determining the index of refraction.

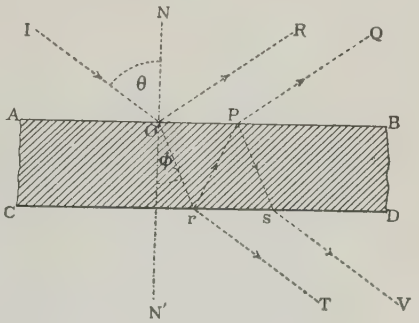


FIG. 596.

When a ray of light strikes a parallel-sided plate of such an isotropic transparent substance, a portion of it is reflected symmetrically to the surface of the plate. This may be otherwise expressed by saying that it is reflected at an equal angle with the normal (the perpendicular to a surface) to the plate. The reflected ray also lies in the same plane as the incident ray and the normal to the surface. These two form the ordinary **Laws of Reflection** of light at a plane surface. Thus in Fig. 596, if IO be the ray incident on the surface AB of the plate ABCD, and NON′ be the normal to the plate, then the ray is reflected along OR, which

follows a direction such that the angle RON is equal to the angle ION, IO and RO being thus symmetrical to the surface AB. The angle of incidence, as also the angle of reflection, is always measured from the normal to the surface, and not from the surface itself. The angle IOA, that measured from the surface, is known as the " glancing angle," and is that referred to in connection with the reflection of X-rays from the planes of atoms in crystals (see footnote on page 649). Perpendicular incidence on a surface is alone reflected back along the same path.

It has also to be remembered that a certain portion of the incident light, the amount depending on the imperfection of the polish of the surface, the roughness or irregularity of the surface, is also reflected irregularly, or " scattered " as it is termed ; and it is by means very largely of this scattered light that we see the object. These miniature innumerable reflections affording the scattered light are only irregular in so far as the surface is irregular ; each minute element or similarly reflecting tiny plane portion of the surface reflects light in accordance with the regular law of reflection just stated, so long as its dimensions are not so small as to be of the order of the wave-length of light.

The incident light is vibrating in every azimuth perpendicular to its direction of propagation, if it be ordinary light. But after reflection at the surface of the plate more or less of it, depending on the angle of incidence, is constrained to vibrate in the plane of the surface, that is, it becomes plane-polarised. For some particular angle of incidence dependent on the substance, 56° 35′ in the case of ordinary crown glass for instance, the whole of the reflected beam, if composed of monochromatic light (sodium light in the case of glass just mentioned), is thus plane-polarised. This angle is known as the " polarising angle."

A great deal of controversy has occurred in the past as to whether the plane of polarisation should be considered as that in which the plane vibrations occur, or the plane perpendicular thereto. It has already been shown that there are effects, both electric and magnetic, in both planes ; and the convention mutually agreed upon by the great majority of physicists, following the assumption of Fresnel, is that the plane of polarisation shall be considered as perpendicular to the plane in which the vibrations occur, that is, to be parallel to the plane of incidence, the plane ION, parallel to the paper, in Fig. 596. It has been so decided on the ground that the direction of vibration follows the electric effect more than the magnetic, and the electric disturbance occurs principally at right angles to the plane of polarisation as understood by Fresnel.

It is thus very important to remember, that when a polarising Nicol prism (our best means of producing polarised light, to be described in Chapter XL.) is arranged with its axis horizontal and its plane of polarisation, the 0°-180° diameter, the longer diagonal of the end-face of the rhomb, also horizontal, and with the 90°-270° diameter, the shorter diagonal, vertical, the transmitted vibrations are occurring vertically ; and when the prism is rotated so that the zero or 180° graduation is at the top of the vertical diameter, the vibrations are horizontal. That is, the diameter which carried the zero mark has to be horizontal in order that

the prism may let through vertical vibrations, and vertical if it be desired to transmit horizontal vibrations. The vibration plane of a "Nicol" (as the Nicol prism is currently termed) is always parallel to the shorter diagonal. Hence vibrations parallel to the refracting edge of a 60°-prism of a birefracting crystal are transmitted when the Nicol is at 90°, and those perpendicular to the edge and bisecting the angle of the prism are transmitted when the Nicol is at 0°, assuming that the prism is arranged on a horizontal-circle goniometer-refractometer with its edge vertical as usual.

The remainder of the light incident on the plate in Fig. 596, and not reflected, penetrates within the glass or whatever transparent material the plate is composed of, and is polarised in a proportion corresponding to that of the reflected light, but in the perpendicular plane, at right angles to the plane of incidence; that is, the vibrations occur parallel to the plane of incidence.

A plate of the mineral tourmaline is well known to act as a very perfect polariser of light, that is, to constrain the vibrations of such light as passes through the tourmaline to confine themselves to a single plane. In the case of tourmaline the direction of this plane is parallel to the trigonal axis of the crystal, tourmaline crystallising in the trigonal system, class 20, the ditrigonal-pyramidal polar class, as shown on page 348 of Chapter XXII. and illustrated in Fig. 300; the crystal plate is generally cut parallel to the trigonal axis for polarising purposes. Now tourmaline is a mineral which possesses in a high degree the property of "pleochroism," that is, it exhibits different absorptive effects on light vibrating along different directions within the crystal (see Chapter LI.). Moreover, as in the cases of all birefringent crystals, the rays of ordinary light are in general constrained when they enter the crystal to vibrate along two directions only, and in this case, being trigonal in symmetry, the two component rays are an ordinary and an extraordinary one in the sense which will be fully explained in Chapter XXXIX. Now, the difference of absorption of these two rays during their passage through the tourmaline crystal structure is so considerable, that the ordinary ray, when the crystal plate is cut parallel to the axis as usual, is practically entirely absorbed before it can emerge, and thus the extraordinary ray, the vibrations of which are parallel to the trigonal axis, is alone transmitted as a perfectly polarised beam of light.

Consequently a plate of tourmaline affords a delicate test for the polarisation of light reflected or refracted from glass, and in the case of the reflected rays, if the angle of incidence be near 56° 35′, they are practically all extinguished by the plate of tourmaline cut parallel to the trigonal axis, when that axis, generally parallel to the longer edge of the plate, is parallel to the plane of incidence; but the refracted rays readily pass through a tourmaline thus held.

It will be obvious also that when two such elongated plates of tourmaline parallel to the axis are held parallel to each other in a beam of light, the latter passes through as a beam of plane-polarised light, and to the eye of an observer on the other side the tourmalines appear transparent, with the slight or deeper colour corresponding to two thicknesses of the mineral; but if the two plates be crossed at right

angles, the overlapping square will appear to the same eye quite black and opaque, the plane-polarised light getting through the first being altogether stopped by the second. When such a pair of plates of tourmaline—now very rare, especially if they are of considerable size, with a minimum of colour, and that pale brown rather than green—are mounted in a manner which permits of their independent rotation, so that they may be arranged crossed to each other or parallel at will, or at any angle of mutual inclination, they form an excellent "polariscope," an instrument consisting of a "polariser," or producer of a beam of plane-polarised light, and an identically similar "analyser," both rotatable. A section-plate cut perpendicularly to the optic axis of a uniaxial crystal, or to the acute bisectrix of the optic axial angle of a biaxial crystal, when placed between the polarising and analysing tourmalines, will exhibit the circular uniaxial rings and rectangular cross of the one, or the biaxial rings and brushes of the other very clearly, when the arrangement is held close to the eye. The tourmalines are usually supported in independently rotatable mounts at the ends of a pair of spring tongs, between which the crystal section can be gripped with sufficient tightness to hold it firmly, as shown in Fig. 597

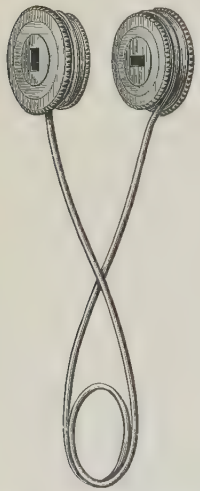


Fig. 597.—Pair of Tourmalines in Pincette.

Two large plates of colourless tourmaline are quite as good as Nicol prisms, and from their increasing rarity are becoming almost as valuable as large Nicols, the Iceland spar for which is now exhausted, only smaller pieces coming into the market, which, however, are adequate for all but projection purposes. The construction of the Nicol prism of Iceland spar will be discussed in Chapter XL., after the doubly refracting peculiarities of calcite have been described in Chapter XXXIX.

Index of Refraction.—The amount of bending or "refraction" of the rays on entering the transparent material depends on what is known as the "refractive index" of the substance. If in our example illustrated in Fig. 596 NON′ be the normal to the plate of glass or other transparent isotropic substance, IO the direction of the incident ray, ION being the angle of incidence, then OR is the reflected portion of the ray, and O*r* the refracted portion. At *r*, where it meets the second surface, it is partly transmitted as the ray *r*T, parallel to the direction of the incident ray IO but no longer in line with it; and partly it is again reflected back to the first surface, which it meets at P; here part escapes as the ray PQ parallel to the reflected ray OR, and part is once more reflected to the second surface at *s*, a portion of this ray then escaping along *s*V parallel to *r*T and part being once more reflected, a ricochet of this kind going on with partial escape of some of the light each time either surface is reached after internal reflection, the escaping ray being obviously weaker and weaker after each successive internal reflection.

Now N′O*r* is the angle of refraction ϕ, and if the angle of incidence ION be represented by θ, then the ratio of the velocity of light in air to that within the crystal is equal to the ratio of the sines of the two angles θ and ϕ, and this ratio it is which is conventionally known as the "refractive index"; it is generally represented by the letter μ when the substance is singly refracting, that is:

$$\mu = \frac{\sin \theta}{\sin \phi}.$$

The refractive index is a constant quantity for light of the same wavelength and for the same two media, but varies with change of either medium. It is a number greater than unity when the medium the refractive power of which is measured by it, compared with that of air, is denser than air; for ϕ will always then be a smaller angle than θ. These facts are combined in the statements of two laws which were established so long ago as the year 1620 by Willabrod Snell, and afterwards restated by Descartes, who thus called more attention to them. They are as follows:

Whatever be the angle of incidence, the ratio which the sine of this angle of incidence bears to the sine of the angle of refraction is constant for the same two media, but varies with different media.

The incident and the refracted ray lie in the same plane, which is perpendicular to the surface of separation of the two media.

Snell's laws apply not only to solids, but also to liquids, and as we shall afterwards require to use liquids of specific refractive powers for various operations in connection with the determination of the optical constants of crystals, it is convenient to include here a list of the refractive indices of a few such liquids which the author has found most useful, together with the indices of refraction of a number of isotropic solid substances, including crystals belonging to the cubic system. All the refractive indices in the two tables refer to sodium D-light and to the temperature of 20° C. The name of the observer is also given in each case.

REFRACTIVE INDICES OF SOME ISOTROPIC SOLIDS.

Fluor spar	1·4339, Fizeau.
Potassium aluminium alum	1·4564, Soret.
Ammonium aluminium alum	1·4594, Soret.
Obsidian	1·4964, Mühlheims.
Sodium chlorate	1·5150, Dussaud.
Crown glass, light Steinheil or Merz	1·5153, v.d. Willigen.
,, heavy Merz or Rosette	1·5339, Mascart.
Rock salt	1·5442, Langley.
Canada balsam (hardened)	1·5450, Schaller and Calkins.*
Flint glass, light Hilger	1·5798, Langley.

* This value is the maximum found for a number of specimens, the variations being from 1·535 to 1·545. As the hardest and densest is most useful to the crystallographer, the highest value probably most accurately represents its index of refraction. Preston (*Theory of Light*, p. 320) states that the refractive index of that used in preparing Nicol prisms is nearly 1·55.

REFRACTIVE INDICES OF SOME ISOTROPIC SOLIDS (*continued*).

Flint glass, heavy Rosette	1·6193, Mascart.
„ very heavy Merz	1·7515, v.d. Willigen.
„ dense Jena, for total reflectometers	1·8904, Pulfrich.
Garnet, colourless grossuralite	1·7438, Wülfing.
„ red almandine	1·8078, Wülfing.
„ green uwarowite	1·8384, Wülfing.
Spinel, chromite	2·0960, Thoulet.
Phosphorus	2·1442, Gladstone and Dale.
Blende	2·3692, Becquerel.
Diamond	2·4669, Schrauf.

REFRACTIVE INDICES OF CERTAIN USEFUL LIQUIDS.

Water	1·3334, Tutton.
Ether	1·3566, Gladstone and Dale.
Ethyl alcohol	1·3616, Ketteler.
Chloroform	1·4462, Lorenz.
Carbon tetrachloride	1·4607, Haagen.
Turpentine	1·4725, v.d. Willigen.
Glycerine	1·4729, Landolt.
Toluene	1·4955, Gladstone.
Benzene	1·5027, Gladstone.
Cedar oil	1·5102, Tutton.
Monochlorobenzene	1·5248, Veley.
Methyl salicylate	1·5363, Wernicke.
Oil of cloves	1·5409, Tutton.
Anis oil	1·5540, Baden-Powell.
Oil of cassia	1·5862, Wiedemann.
Oil of cinnamon	1·6190, Tutton.
Carbon bisulphide	1·6276, Ketteler.
Acetylene tetrabromide	1·6380, Weegmann.
α-Monobromonaphthalene	1·6657, Tutton.
Methylene iodide	1·7421, Gladstone.

Total Reflection and Relation of its Critical Angle to Refractive Index.—If we try to follow what happens when the angle of incidence becomes greater and greater, we shall find that more and more light is reflected, and such lesser quantity as is refracted becomes relatively more and more powerfully refracted, as it approaches horizontal incidence (parallel to the plate surface), just as the converse is true that when the incidence is normal there is no refraction at all, and very little relatively for a small angle of incidence. When the limiting case is reached, and the angle of incidence is actually 90°, the ray thus gliding along the surface has no tendency to enter the denser medium at all. Incident rays, however, falling on the surface at angles just less than 90°, will be refracted partially, although mostly reflected, and the angle of refraction will be the maximum possible. If, now, we approach from the other side and investigate the case of a ray travelling **within** the denser medium towards the limiting surface, such as our plate of glass or other isotropic substance or a transparent liquid, we find that if this ray meet

the second surface of the plate, or the surface of the liquid, at the maximum angle just referred to, it will partially emerge; but if the angle be not only just greater than that maximum angle for emergence, but also exceeds that which would produce the gliding along the surface, corresponding to 90° of incidence, it will not emerge at all, as the ray rT is shown as doing in Fig. 596, but will be totally internally reflected at the surface, back within the denser medium again, at an angle equal to that of this interior incidence. When the interior ray AO meets the surface exactly at the "critical angle," it glides along the surface OB, as shown in Fig. 598.

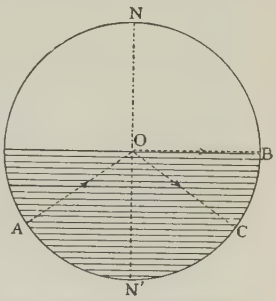


FIG. 598.—Total Reflection at the Critical Angle.

Expressing the facts mathematically, if θ be the angle of incidence as before, then $\theta = 90°$ for the critical angle of refraction, which latter we term ϕ as before, maintaining the same conventional signs throughout. This critical angle of refraction ϕ is now the interior angle of incidence. Then:

$$\mu = \frac{\sin\theta}{\sin\phi} = \frac{\sin 90°}{\sin\phi} = \frac{1}{\sin\phi},$$

or

$$\sin\phi = \frac{1}{\mu}.$$

Thus the sine of the critical angle is equal to the reciprocal of the refractive index. As the latter differs for light of different wave-lengths, the critical angle also varies with the wave-length. This is the law of total reflection, of which great use will subsequently be made in crystal optics. It means that if a ray AO (Fig. 598) be incident within the transparent solid or liquid at an angle the sine of which is equal to the reciprocal of the index of refraction, the ray never gets out, but is reflected along the surface OB, and the least increase of this angle causes the ray to be totally reflected at the limiting surface of the two media, at the same angle OC, back again within the substance.

Determination of the Refractive Index by the Total Reflection Method.—The important law just stated is the foundation of the total-reflection method of determining the refractive index by means of the total-reflectometer. The instrument and the actual mode of carrying out the determination will be described in Chapter XLVII. For the limit at which total reflection begins is so sharp that by a suitable method of observation it can be caused to take the form of a straight or regularly curved line of demarcation between an illuminated part of the field of view of a telescope and a dark portion, so sharp, indeed, that the limiting line can be adjusted to a cross-wire in the eye-piece of the telescope of the total-reflectometer. The latter being merely a specially modified goniometer - refractometer, the critical angle is thus measured directly by the divided circle. The refractive index μ is afforded by the expression:

$$\mu = \frac{1}{\sin \phi},$$

where ϕ is the critical angle. That is, we have merely to calculate the reciprocal of the sine of the observed critical angle.

The critical angle for water to air for sodium light is 48° 35′, corresponding to the refractive index for 20°, 1·3334. That from glass to air, also for sodium light, is 41° 18′ for light crown glass of refractive index 1·5153, and 39° 16′ for light flint glass of refractive index 1·5798.

Application of Total Reflection to the Right-angled Prism.—An important further application of the principle of total reflection, with which we shall have to deal in experimental crystal optics, is in the right-angled total-reflection prism. It is a prism formed by three faces, the plan of which is an isosceles triangle, the two equal faces being perpendicular to each other, so that the other two angles of the prism are 45°, as illustrated in Fig. 599. All three surfaces are polished, and truly plane if required for accurate work of the kind we shall have to describe later on. The main use of the prism is for reflecting a beam of light at right angles to its original path. One of the rectangular faces *abcd* is arranged normally to the direction of the beam, and the latter then passes in the direction of the arrow through this face undiverted by any refraction straight to the hypotenuse-face *bcef*, striking the latter, say, about its centre; it does so obviously at 45°, which is larger than the critical angle for glass. For this has been shown to be 41° 18′ for light crown glass and 39° 16′ for light flint glass, so that we may expect the glass of which the prism is made to have a critical angle somewhere between these limits. It is, therefore, totally reflected at the hypotenuse, and thus strikes the second rectangular side *adef* normally, so that it is transmitted out into the air again without refraction or other diversion, thus emerging at right angles to the original direction, and without further loss of light than the minute amount due to absorption by the glass and that due to normal reflection.

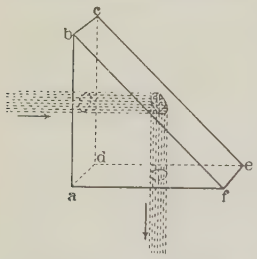
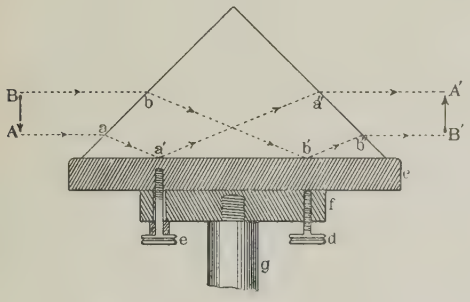


FIG. 599.—Principle of the Right-angled Totally-reflecting Prism.

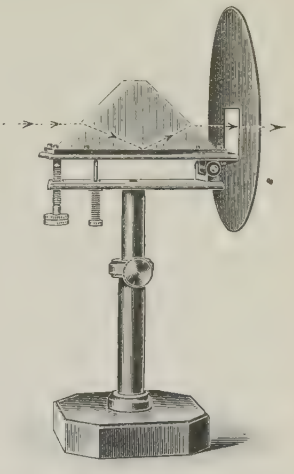
When used in another manner which is shown in Fig. 600 the right-angled reflecting prism is known as an "**Erecting Prism**," as it inverts the rays passed through it, so that if a beam of light passing to the screen in a projection experiment, and producing there as usual an inverted image of the object projected by the lens, is passed through such an erecting prism, the image is reinverted by it and thus rendered upright on the screen. In the ordinary projection of lantern slides the slide is placed inverted in its carrier in the lantern front, in order that its enlarged image may be upright on the screen. But when an experiment is being projected, the apparatus being arranged between the lantern condenser and the projecting lens, it is rarely convenient to place it upside down, and here the use of an erecting prism is invaluable. The prism rests on its base, which is either horizontal or tilted slightly parallel to the beam of light when the latter is not quite horizontal; the means of tilting are provided in the form shown at A in Fig. 600 by the three levelling or adjusting screws for the supporting table *c* on which it rests, one of these screws being shown at *d*, while three other fixing screws, one shown at *e*, serve rigidly to fix the table, if necessary, after adjusting. The adjusting screws *d* screw through the under fixed table *f*, but do not enter *c*; while the fixing screws *e* pass easily without screwing through *f* but screw into *c*. The supporting column *g* passes down into a suitable pedestal, in the

column of which it is adjustable for height and is also of course rotatable. Hence all necessary adjustments are very simply provided for. A still simpler mode of adjusting the prism is shown at B in Fig. 600, a screen with central aperture being also provided in order to exclude all rays but those of the desired beam.

A beam of light AB (see Fig. 600) passing from the lantern to the screen enters the prism at *ab*, where it is refracted. Considering first the ray A, after refraction at *a* it is totally reflected at *a′* from the polished base of the prism (all three faces being polished) and leaves the prism at *a″*, where a second refraction brings it parallel to its original direction but on a higher level. On the other hand the ray B suffers the two refractions *b* and *b″* and the reflection at *b′*, and emerges after the second refraction at *b″* parallel to its original direction but at a lower level. If the arrow at AB represent the inverted image of the object placed between the lantern condenser and the projecting lens, then after traversing the erecting prism it appears on the screen erect as A′B′.



A.—Principle of the Erecting Prism.



B.—Erecting Prism on Adjustable Stand as used for Projection.

FIG. 600.—The "Erecting Prism."

Sometimes this erecting prism is given a larger angle than 90°, a common one being 105°. It will be observed that the upper or apex portion of the prism is not used; hence, to save glass, this upper part is often cut away, as shown at B in Fig. 600.

Dove's Prism is a right-angled erecting prism constructed of Iceland spar, calcite (calcium carbonate, $CaCO_3$), which acts as an ordinary erecting prism, as above described, for the "ordinary" ray, while the "extraordinary" ray, the second of the two rays into which a beam of light is divided on entering a doubly refractive crystal such as calcite (as will be fully explained in Chapter XXXIX.), is not totally reflected but largely passes out of the base and is absorbed by lamp-black paint on the supporting table or other mount. It thus gives an erected (reversed) image in polarised light, the plane of polarisation of which is that of the "ordinary" ray of calcite. One often hears the common glass erecting prism referred to as a "Dove's prism"; strictly speaking the name only applies to one of calcite. The spar is cut so that the optic axis is parallel to the receiving face of the prism, and perpendicular both to the exit face and to the apex-edge between these two faces.

Fresnel's Rhomb.—This is a simple device for utilising the principle of total reflection for the production of circularly polarised light (see page 909 and Fig. 666). It was devised by Fresnel as the result of his mathematical conceptions in connection with the undulatory theory of light, and verified his expectations to the fullest extent. It consists of a rhomb of glass with parallel faces (parallelepiped), *a*, *b*, *c*, *d*, in Fig. 601,

so disposed that a ray of light entering normally at one of the two narrower faces is totally reflected internally at each of the longer parallel pair of faces, that is, p and s, and leaves the prism normally to the other narrow end face; the acute angles of the rhomb are made to be as near 54° 37′ as possible. The rays are thus incident on the first reflecting face at an angle of 54½°, and are there totally reflected; they strike the second long face at the same angle and are again totally reflected, and emerge parallel to their original direction but somewhat laterally displaced. At both p and s a difference of phase of 1/8th-wave retardation is produced, that is of 45°, and the sum of the two retardations is consequently 90° or one-quarter wave. If the ray be originally polarised, say by a Nicol prism, and its plane of vibration be arranged to be inclined 45° to that of reflection (the plane of the paper in Fig. 601), its components in and perpendicular to the plane of incidence and reflection will be equal, and the emergent light will therefore be circularly polarised. The rhomb answers perfectly to the test, and circularly polarises rays of all wave-lengths equally, so that it is particularly useful with white light; in this respect it is superior to a quarter-undulation plate of mica (see page 909), which strictly effects its purpose for one wave-length only. A quarter-wave mica plate, on the other hand, is very convenient as occupying practically no space, and producing no displacement of the ray. This latter is especially troublesome when the rhomb requires to be rotated. The rhomb may be also used to convert circularly polarised light into linearly polarised light; for on passing a circularly polarised beam through it a further difference of phase of 90° is introduced, so that the emergent beam is plane polarised. If a ray of light originally polarised at 45° azimuth be passed through a succession of Fresnel's rhombs, the issuing light will be either circularly or linearly polarised according as the number of rhombs is odd or even. The rhomb also converts elliptically polarised light into plane polarised, when the rhomb is so arranged that the major and minor axes of the elliptic vibration are in and perpendicular to the plane of incidence (plane of the paper in Fig. 601) respectively.

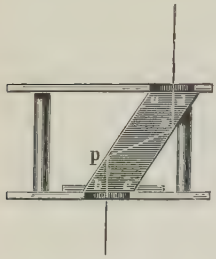


FIG. 601.
Fresnel's Rhomb.

Determination of Refractive Index by the 60°-Prism Method.—By far the most convenient and accurate method of measuring the refractive index is by observation of the refracted images, in various colours of light, of the collimator slit of a refractometer-goniometer through a 60°-prism, the method, in fact, of producing a line-spectrum, the lines of which, of known specific wave-lengths, give us the means of determining the refractive index for definite radiations.

As the source of light, we may employ sunlight when available, when we have the Fraunhofer dark lines as known particular wave-length radiations. A heliostat, however, is necessary with sunlight, to keep the image of the sun constantly on the slit, and there is besides the liability to interruptions by clouds to be considered. Hence, we may much more conveniently employ the bright lines of metallic vapours, such as those of sodium, lithium, and thallium, the respective yellow, red, and green lines of which are particularly convenient for the purpose. Or again, we may employ a hydrogen Geissler vacuum tube, and raise the residual hydrogen gas, at the exceedingly low pressure left in the tube, to incandescence by means of the high tension intermittent electric discharge from the secondary circuit of a Ruhmkorff induction coil, and thus produce the primary spectrum of three bright lines of hydrogen, the red C, the greenish-blue F, and the violet line near G. Or, best of all, we may employ the author's

spectroscopic monochromatic illuminator, described in Chapter XLIV., which supplies monochromatic light to any instrument whatsoever, and to the goniometer-refractometer especially well on which the 60°-prism is to be measured as regards both its refracting angle and the angle of deviation of the rays transmitted by it. The monochromatic light furnished by this instrument is of such purity that only a 250th part of the spectrum is included, the position of which, moreover, and the actual wave-length, it directly affords, and which may be any desired wave-length whatsoever.

If in Fig. 602 ABC be the section of a 60°-prism by a plane perpendicular to the faces, the refracting edge being at C, a ray of light refracted through it obviously cannot emerge parallel to the original direction however the prism may be arranged, for this only occurs with a parallel-surfaced plate. But the amount of deviation is not constant for all positions, but has a minimum when the path of the refracted ray through the prism is parallel to the side AB of the prism opposite to the refracting angle, and to the basal plane on which the prism stands, parallel to the paper in Fig. 602; the incident and emergent rays then make equal angles with the two refracting faces of the prism. This symmetrical position of "minimum deviation" can be very readily found in practice, when the prism is mounted on the crystal-adjusting apparatus of the goniometer-spectrometer, and thus the method is particularly convenient and accurate.

The collimator and telescope are first arranged in the same straight line, and the direct reading of the Websky slit-signal as observed through the telescope is taken on the circle; the telescope is then rotated to one side, the collimator and divided circle remaining clamped together and fixed to the tripod base, until by suitable rotation of the prism, the crystal axis being left loose, the refracted image of the signal-slit is seen directly by the eye, broadened into a spectrum by the different refraction or "dispersion" of light of different wave-lengths. It will then be found that when the arrangement is as shown in Fig. 602, rotation of the prism in either direction causes the spectrum-image of the slit to move in that one and the same direction which, if the telescope followed it in order to measure the angular movement, would increase the angle of deviation of the light rays, from the original position of the telescope for the direct reading on the circle, when it was in line with the collimator. The prism is then rotated back to its position corresponding to minimum deviation, and the telescope arranged so that the spectrum-image for this position is adjusted as nearly as a broad spectrum can be to the cross-wires. The least turn of the prism either way causes the image to move away from the vertical cross-wire, and on that side of it in either case which would increase the angle. After thus preliminarily adjusting the spectrum-image in white light with the ordinary goniometer lamp, the final adjustment must be made in monochromatic light, preferably sodium light, which is a radiation in a conveniently central part of the visible spectrum. The angular difference between this adjusted position and the direct reading is the desired angle of minimum deviation. Similar measurements are then made for all the radiations for which it is desired to determine the refractive index, the adjustment of the setting to minimum deviation being verified and made perfect for each colour, as tested by verifying that on movement of the prism in either direction by rotation of the crystal-holding and adjusting axis supporting it, no further approach of the image towards the direct reading occurs, and if any further slight adjustment be required, as is usual for the two ends of the spectrum, it is made in each case.

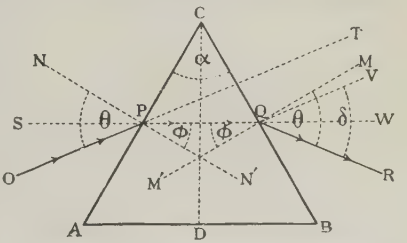


FIG. 602.—60° Refracting Prism arranged for Minimum Deviation.

By using the author's spectroscopic monochromatic illuminator described in Chapter XLIV., determinations of minimum deviation for six or more wave-lengths of light can be very rapidly carried out. The author usually employs those corresponding to red Li-light, red C-hydrogen light, yellow sodium light, green thallium light, greenish-blue F-hydrogen light, and violet hydrogen light near G. The only other measurement required is that of the refracting angle of the prism, which is measured in the usual goniometrical manner. (See Chapter XLVI. for practical details.)

The calculation of the refractive index is exceedingly simple from the data thus acquired, namely, from the angle δ of minimum deviation for a number of different wave-lengths of light, and the internal angle of the prism α, which is somewhere in the neighbourhood of 60°, and is, of course, determined to a single minute of arc.

Now if OP in Fig. 602 be the incident ray, PQ the direction of the refracted ray through the prism at minimum deviation, and therefore parallel to the third side of the prism AB opposite the refracting angle ACB, α; and if also QR be the emergent ray, NPN′ and MQM′ the directions of the normals to the prism faces employed, and CD the plan of the bisecting plane of the prism; then, the angle of incidence OPN is equal to the angle RQM made by the emergent ray with the normal to the second surface. Let this angle of equal incidence and emergence be termed θ, as usual for an angle of incidence in the nomenclature of this book. Then the angle of refraction QPN′ is equal to the angle PQM′. Let these be called ϕ, in accordance with our usual labelling of an angle of refraction.

Now we have seen that the index of refraction μ is the quotient of the sine of the angle of incidence by the sine of the angle of refraction, that is:

$$\mu = \frac{\sin \theta}{\sin \phi}.$$

But by the principle of similar triangles, PQ being normal to CD and NPN′ to AC, the angle of refraction ϕ is equal to $\frac{\alpha}{2}$. Also the angle of incidence θ is made up of the two triangles NPS and SPO. But NPS is equal to ϕ, that is, to $\frac{\alpha}{2}$, and SPO is equal to half the angle δ of minimum deviation, that is to $\frac{\delta}{2}$. For the angle of minimum deviation δ is the angle between the direction of the incident ray OPT—which is that of the direct reading of the slit image—and the direction of the emergent ray QR. If we draw QV parallel to OPT, the angle VQR is the angle of minimum deviation δ in question. Now, as the angle WQR, part of this, is equal to SPO, and the angle WQV, the other part, is also obviously equal to SPO by construction, the whole angle δ of minimum deviation RQV must be double of the angle SPO, that is, $\text{SPO} = \frac{\delta}{2}$.

Hence, the whole angle θ of incidence NPO is the sum of half α and half δ, that is:

$$\theta = \frac{\alpha}{2} + \frac{\delta}{2} = \frac{\alpha + \delta}{2}.$$

Consequently, the refractive index μ, which by definition $= \frac{\sin \theta}{\sin \phi}$, is represented by the expression:

$$\mu = \frac{\sin \frac{\alpha + \delta}{2}}{\sin \frac{\alpha}{2}},$$

Thus **the refractive index is equal to the sine of half the sum of the**

angles of the prism and of minimum deviation, divided by the sine of half the prism-angle.[1]

Relation between Refractive Index and the Polarising Angle.—As we now thoroughly understand the meaning of refractive index and its mode of practical determination, we are in a position to inquire more closely as to its relation to the most favourable angle for the complete polarisation of a ray reflected from the plane surface of a transparent solid.

An extremely simple law was discovered by Brewster to apply, namely, that **the polarising angle is that angle the tangent of which is equal to the index of refraction.**

If in Fig. 603 XOX′ represent the surface of the glass plate and YOY′ the normal to the plate, and if AO be the incident beam and θ the angle of incidence AOY, then OB is the direction of the reflected ray, making also the angle θ with OY. Now Brewster found experimentally that to produce the maximum polarisation the angle AOY must be such that the direction of the refracted ray OC within the glass (COY′ being the angle of refraction ϕ) must be at right angles to the reflected ray OB.

Hence the index of refraction μ becomes :

$$\mu = \frac{\sin\theta}{\sin\phi} = \frac{\sin\theta}{\sin(90^\circ - \theta)} = \frac{\sin\theta}{\cos\theta} = \tan\theta.$$

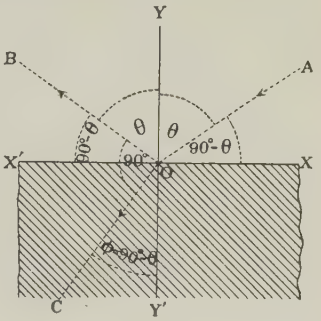


FIG. 603.

That is, **the index of refraction is equal to the tangent of the angle of incidence when maximum polarisation occurs.**

Hence, if we look out in a book of mathematical tables the angle the tangent of which corresponds to the refractive index, which is known, that angle is the most favourable angle for polarisation by reflection.

The polarising angle may be also stated as **that angle of incidence for which the reflected polarised ray is perpendicular to the refracted ray.**

This law is absolutely true only for light of a specific wave-length, light of each wave-length having its own polarising angle.

In the following table are given the polarising angles, using sodium light, for crown and flint glass, and for natural glass, obsidian, which is much used in making the plates for glass polarisers ; also for water, the still surface of which is effective as a polariser at an unusually low angle, corresponding to the low refractive index ; and for diamond, the angle of polarisation of which is very large on account of its extremely high refractive index.

[1] The absolute refractive index *in vacuo* is obtained by applying a correction for the refractive index of air relative to a vacuum, which is 1·00029. The correction amounts to +0·0004 for refractive indices from 1·30 to 1·57, +0·0005 for indices beyond this up to 1·89, +0·0006 for indices higher than this up to 2·21, and +0·0007 for still higher indices up to that of the diamond (2·4669).

Polarising Angles for Na-light.

	Refractive Index.	Polarising Angle.
Water	1·3334	53° 8′
Obsidian, natural glass .	1·4964	56 15
Light crown glass . .	1·5153	56 35
Light flint glass . .	1·5798	57 40
Diamond	2·4669	67 56

Dispersion.—The fact that the refractive index of a solid, liquid, or gaseous substance, that is, of any material substance, is different for light of different wave-lengths, is clearly exhibited by the results of the determinations of refractive index by the 60°-prism method. That the difference is a regular one is also demonstrated by the production of a definitely graduated coloured spectrum by such a prism, the colours following the order of the wave-lengths, red being at the least refrangible end and violet at the most refrangible end of the spectrum.

It was with the aid of a glass prism of somewhere about 60° angle that Newton first discovered the composite nature of the white light of the sun, and showed that the different colours are deviated to different amounts by transmission of the beam of white light through the prism, and that it may be projected as a spectrum on a white screen. This inequality of refraction of the various colours of light, or more properly expressed, of light of the progressively varying wave-lengths, due to the regular progression in refrangibility as the wave-length changes, differs in its amount in different media, and the difference is expressed by the relative length of the spectrum, or, as it is called, the "**dispersion.**"

That this difference of refrangibility for different wave-lengths is a truly progressive property is shown by the fact that the refractive index μ can be expressed by a general formula for any wave-length λ, the well-known formula of Cauchy,

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ \ldots\ ,$$

where A, B, C are constants special to the medium, the substance of the prism. This formula expresses the fact that waves of short period and wave-length are more highly refracted than those of longer period, and that the inferior limiting value is $\mu = A$, when the wave-length becomes theoretically infinite, and the second and third terms zero in consequence. The formula, when used to the extent of the three terms quoted above, expresses the results for the visible spectrum very accurately, but fails when an attempt is made to extend its application to the dark infra-red radiations and those of radiant heat. The practical application of the formula will be found described and illustrated in Chapter XLVI. The mode of finding the constants A, B, and C, by use of the results for the three wave-lengths corresponding to the red hydrogen line C, the yellow sodium line D, and the green thallium line, will also be described.

The explanation of this important property of **Spectral Dispersion** is given by Preston [1] as follows. Rays which are refracted by different amounts on entering any medium must travel through that medium with different velocities, the relation between the absolute refractive index (the refractive index of the substance *in vacuo*, about 0·0004 greater than that for the substance in air) and the velocity for any ray being $\mu = \frac{v_0}{v}$, where v_0 is the velocity *in vacuo*, free space, that is, in the ether, and v is the velocity in the substance. The velocity v_0 is the same for light of all colours. For dispersion does not exist in free space, but is entirely a phenomenon arising from the interaction of matter and the ether of space. The constancy of v_0 for all waves of the visible spectrum, from red to violet, has been proved from astronomical considerations concerning regularly variable stars. From all these facts Cauchy showed that the velocity will in general be a function of the wave-length λ, and he arrived at the following formula expressing the fact:

$$v^2 = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} + \frac{d}{\lambda^6} + \ . \ . \ . ;$$

from which it follows as regards the refractive index μ that:

$$\mu = \mathrm{A} + \frac{\mathrm{B}}{\lambda^2} + \frac{\mathrm{C}}{\lambda^4} + \ . \ . \ . \ ,$$

which is the formula already referred to as expressing the refractive index μ for any wave-length λ.

A formula expressing still more closely the facts for the visible spectrum, and which also holds good for the dark rays of the infra-red, is the following, due to Briot: [2]

$$\frac{1}{\mu^2} = \kappa\lambda^2 + \mathrm{A} + \frac{\mathrm{B}}{\lambda^2} + \frac{\mathrm{C}}{\lambda^4} + \ . \ . \ .$$

Briot showed that matter affects the ether in two ways: firstly by modifying its distribution in the body, which gives rise to the Cauchy series, and secondly by exercising a direct action on its motion when vibrating, which introduces the term $\kappa\lambda^2$.

Diffraction.—It has already been mentioned on page 794 that the fact that light waves are not infinitely small, but have an appreciable length, varying from 0·0004 to 0·0008 millimetre, is responsible for the phenomenon of diffraction, exhibited when light is incident on a very sharp edge or succession of edges, such as the two fine edges of a narrow slit, the striæ on a striated crystal-face, or the "rulings" of a diffraction grating.

For the light waves do show some deviation from the rectilinear course in passing by the edge of an opaque obstacle, and to the extent which could be expected from the minute length of the waves; that is, they do bend round an adequately sharp corner, and instead of going on in the original straight path they diverge to the extent to be expected. Also when the light waves pass through a very small aperture, comparable

[1] *Theory of Light* (Macmillan & Co.), p. 485.
[2] Essai sur la théorie mathématique de la lumière, Paris, 1864.

in size to the wave-length, they do not emerge as a sharp line, ray, or pencil of light, but diverge in all directions. Such deviations give rise to the phenomena of iris-coloured diffraction fringes, both rectilinear and circular, and the many observed beautiful complicated patterns, dependent on the shape of the orifice, edge, or fine obstacle.

The principle may be well illustrated by concentrating the light from an electric arc lantern on a very narrow slit, A in Fig. 604, which may subsequently be considered as the source of light. If another slit B, opened wide, say to about an inch of opening, be placed at a distance of 7 or 8 feet from the narrow slit A, and in the beam or cone of light from the latter, and the light passing through this wider slit B be allowed to reach the usual lantern screen C, the two borders *bb* of the light patch on the screen, the shadows of the edges of the slit B, will be seen to be quite sharply defined. But if now the slit B be narrowed, as indicated at B′, the new boundaries *b′b′* are observed to be no longer sharp.

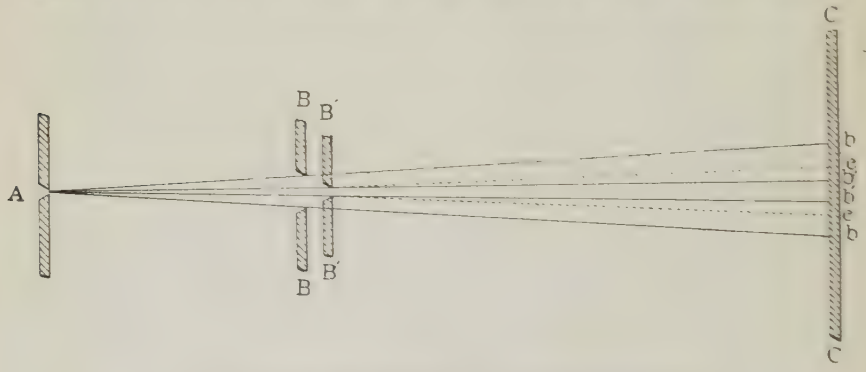


FIG. 604.—Experiment illustrating the Principle of Diffraction.

but to be diffused to *c* and coloured, owing to the bending of the light waves round the sharp slit-edges into the shadow which geometrically from the rectilinear propagation of light—should be expected, and to the presence of but little unaffected and irradiating white light coming through to illuminate the shadows. The narrower the slit B is made, the more diffuse and brightly coloured is the line of light along its edges, and under the best conditions three distinct iris-coloured fringes are seen passing into the shadow on each side.

It is particularly interesting to use two slits instead of one at B, as then in addition to the bending of the rays we have also the interference of the light from the two slits coming into play, producing interference bands, the separation of which from each other is the greater the closer the two slits are to each other. If the number of slits at B be multiplied we obtain the effect of a diffraction grating, there being produced a central sharp white image and a separate spectrum-image on each side of it, that is, an image showing no white illumination but instead all the colours of the spectrum in their proper wave-length order.

Lord's Rayleigh's Interference Apparatus.—A simple but very effective arrangement, on the lines of the two slits at B just referred to, for producing interference bands has been devised by the late Lord Rayleigh, which is equally good for eye vision or screen projection. It consists, as originally constructed by Lord Rayleigh (the author possessing one of these effective little instruments, by the kindness of the present Lord Rayleigh), of a cardboard tube 1 foot long and $1\frac{1}{8}$th inch outside diameter, blackened inside and closed at each end with an opaque diaphragm. That at one end is simply a metallic disc pierced by a slit, which is 16 millimetres long and slightly over half a millimetre wide in opening. At the other end the closure is effected by a silvered glass mirror, with reflecting side facing outwards but protected by the glass; in the silvering two very fine parallel lines 8 mm. long are ruled, cutting quite through the silver, and about one-tenth of a millimetre apart. On looking up to a bright sky (best with white clouds) through the tube, with the double line (pair of fine slits) nearest the eye and the coarse slit end directed at the sky, the bands, a dozen or more of them according to the illumination, are seen quite clearly, spaced parallel to each other at regular intervals apart. Fig. 605 will afford some idea of them in black and white. Those in the centre are nearly black with coloured margins, but the intensity fades off on each side with every successive band more and more, while the iris coloration becomes at first more marked, then in turn fades off. If directed at or very near to the sun at least seven bands on each side of the central band or pair of bands can be seen. In monochromatic light, directed at a sodium flame for instance, the bands are black, deepest at the centre of the series, on a ground of the colour of the light used. For projection purposes it is only necessary to arrange the tube in the axis of a suitably narrow beam from the condenser of an electric lantern, and to follow it with a projection lens to project the image of the interference bands on the screen. The latter requires to be fairly close and the image to be not too large, as the amount of light transmitted is obviously small. The screen image can be obtained quite large enough, however, say one to two feet square, to be clearly visible to a small audience.

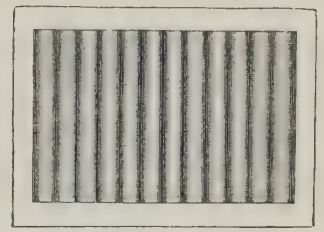


FIG. 605.—Diffraction Bands as afforded by Lord Rayleigh's Apparatus.

Fresnel's Bi-prism.—The well-known method of obtaining interference bands and projecting them on the screen by means of Fresnel's bi-prism should also be mentioned. The bi-prism is simply a glass prism of isosceles triangular section, but in which the two equal sides are so obtusely inclined as to form almost the same plane, the angle only differing by a very few degrees from 180°; in other words, it is an exceedingly low and therefore very thin prism. The best size for projection purposes is about 2 inches square, and it is mounted at the centre of a circular screen, with suitable square aperture for the purpose, carried on a firm stand adjustable for height. An achromatic projecting lens of about 8 inches focus and $3\frac{1}{2}$

inches diameter is most suitable for projecting the interference fringes on the screen. A slit replaces the ordinary lantern projection lens on the optical front of the lantern, and the object stage of the latter is advantageously occupied by a large cylindrical lens of 5 inches focus to condense a parallel beam of light from the ordinary lantern condenser on the slit. From the slit the light diverges upon the bi-prism, which has its basal face turned towards the lantern to receive the rays, and perpendicular interference fringes (parallel to the refracting edge, the upright middle line, of the bi-prism) appear on the screen, and can be made clearer and sharper by interposing the achromatic projecting lens so as to focus them on the screen.

The theory of the bi-prism is simply that it behaves like two adjacent prisms of very small angle, the rays through which are refracted at a very small angle to each other. The object projected being a slit, the two sets of rays behave as two very near slit origins, and interfere as in the two-slit experiment.

The Diffraction Grating.—It has been mentioned on page 387, in the section concerning striated crystal faces, that a very finely striated face acts like a diffraction grating, affording instead of a single white-light reflection of the goniometer signal a central widened white image and a series of spectra on each side. The diffraction grating, as used in spectroscopy, is a finely polished surface of either glass or speculum metal ruled by a fine diamond point at perfectly regularly spaced intervals with a vast number of truly parallel lines, the most useful number being about 14,000 or 15,000 to the inch. It may be likened to a series of parallel bars (the opaque rulings on the glass plate, or the non-reflecting grooved rulings on the speculum metal) regularly arranged very close together, which stop the light rays actually striking them, while the rays arriving opposite the intervals between them (the clear glass interspaces or the reflecting interspaces of polished speculum surface) are permitted to pass through or to be reflected. Each interval may be considered as a source of light. A transparent replica cast in celluloid, such as are made by Thorpe of Manchester, of one of Prof. Rowland's speculum metal 14,000-lines-to-inch gratings, with 14,435, 14,438, 14,472, or 14,486 lines to the inch, forms an excellent grating for experimental purposes at a comparatively slight cost, for use either by transmission or reflection.

From each of the separate interval-sources the light spreads out (is diffracted) in circular waves. If the incident wave be plane, and if it fall normally on the grating, all the waves obviously start from the rectilinear openings (or lines of reflection) in the same phase of vibration, and a plane wave parallel to the grating is produced and travels in the direction of the normal to the grating. It may be brought to a focus (affording an image of the source of light) by a lens, on a suitably arranged screen. But if the direction of the light from the succession of centres be not normal to the plane of the grating, as in Fig. 606, in which AB represents the plane of the grating and AC the direction of the light, then from the separate centres B, *a*, *c*, *e*, etc., we have a succession of spherical waves starting in the same phase, and such that if *ab* represent

one whole wave, then B represents no difference, *cd* represents two whole waves difference, *ef* represents three whole waves difference, and so on, the light from each successive opening being retarded one whole wave behind that from the previous opening nearer B. A lens will again bring them to a focus in an image of the source of light, but as the wave-lengths are different for different colours it will only do so for the monochromatic light corresponding to the exact wave-length *ab*. In white light, therefore, the grating will bend the light of the different colours at different angles, the shorter blue rays least, and the longer red rays most, producing a spectrum.

Moreover, if the inclination of AC to AB be such that the light from the successive openings differs by two whole waves we shall again obtain an image in monochromatic light, and a corresponding spectrum in white light, and this spectrum is said to be of the second order. Similarly, at yet another angle AC of reflection or transmission with respect to the plane of the grating AB the difference of phase of successive elements

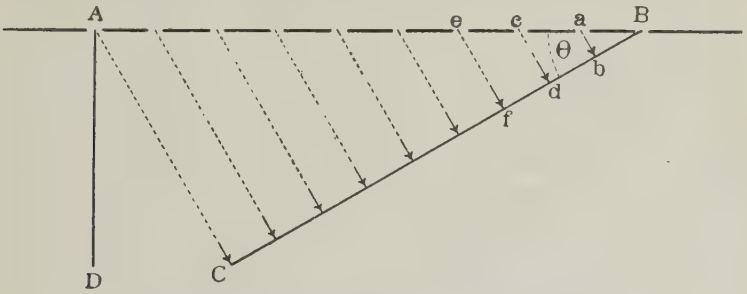


FIG. 606.—The Principle of the Diffraction Grating.

will be three whole waves, and another spectrum, of the third order, is produced; similarly, up to the *n*th order. These specific angles of diffraction θ may be represented in general form as θ_n.

A coarse grating of 600 rulings to the inch will afford, in the same field of view, the central white-light image of the slit and three orders of spectra on each side of it. But a fine grating, such as the Rowland grating of 14,000 lines to the inch or its Thorpe replica, will produce much greater separation of colours (dispersion), the rule being, the finer the ruling the higher the dispersion; and the large Rowland concave gratings used in spectroscopic research, with 20,000 lines to the inch, afford first order spectra as much as four feet long. Moreover, such a grating spectrum has the great advantage over a prismatic spectrum that when the angle of diffraction is small the dispersion is regularly proportional to the wave-length for the different colours, that is, the red end is not relatively crowded together and the blue end relatively more diffused, as it usually is in the spectrum produced by a prism. The spectrum, up to and including that of the third order, is also pure, there being no overlapping or mixture of colours. Hence, the standard spectrum is that produced by a grating.

If the total number of openings (spaces between the opaque or

unreflective rulings) in the grating be N, then there will be N whole waves between A and C (Fig. 606), the total difference of path ; this corresponds to the first order spectrum. The second order spectrum will correspond to 2N waves, the third order spectrum to 3N waves, and the nth order spectrum to nN waves. The efficiency (resolving power) of the grating depends on the order n of the spectrum and the total number of lines N in the grating, that is, it depends on nN. The spectra beyond that of the third order, however, begin to overlap, and do so more and more as the order progresses, so that to obtain a pure spectrum, such as has been commended above as a standard, the order must be low, usually the first, but not superior to the third. The light intensity also diminishes rapidly as the order increases, the first order spectrum being by far the brightest. All these considerations require to be borne in mind, therefore, in choosing a grating spectrum for use in any specific research.

The diamond point, and also the personal equation of the maker of the grating, have much to do with the nature of the spectrum obtained. Occasionally a diamond, by chance, is obtained which rules a grating, in the hands of a certain skilled maker, affording a second order spectrum of maximum brightness instead of giving as usual a pre-eminently bright first order spectrum. Such gratings are highly prized, for a diamond which enhances the order of the spectrum (but not beyond the third) into which maximum light is condensed, and especially one which throws practically all the light into that one higher order spectrum, is producing a grating of maximum possible efficiency.

As already stated, the material on which the rulings are made may be either plate glass (truly parallel surfaced) or finely polished speculum metal, and the ruling machine is provided with a very accurate number-recording apparatus. Rulings have been made on speculum metal so fine and close as to present no less than 120,000 lines to the inch, by the late Prof. H. J. Grayson of Melbourne, and the author has experimented for the purpose of the work in connection with the Imperial Standards of Length (see Chapter LVIII.) with a great variety of Prof. Grayson's rulings, especially those of 40,000, 50,000, and 60,000 lines to the inch ; they have been ruled also on other substances besides glass and speculum metal, namely, on gold, platinum-iridium, Baily's metal (16 parts copper, $2\frac{1}{2}$ parts tin, and 1 part zinc), and invar (nickel steel). Those of 120,000 to the inch afford the limit of microscopic resolution, with the highest power objectives yet constructed. Those of 60,000 are resolvable with a 1/15th inch immersion objective, and even with the dry objectives of that power specially constructed by Mr. Conrad Beck for the two microscopes of the wave-length comparator designed by the author for the Standards Department of the Board of Trade (see Chapter LVIII., Fig. 902). The rulings of 40,000 to the inch on speculum metal are so readily resolved by the two microscopes in question that the lines appear as sharply defined as spider lines, and any one ruled line can be readily brought and adjusted midway between the two parallel micrometer-spider lines of the microscope, and a portion of clear white interval be left on each side of each of the two spider lines.

It is interesting to remember that $\frac{1}{40000}$ inch is the wave-length of red light. For that of red hydrogen C-light is $\frac{1}{38710}$ inch, and that of red cadmium light is $\frac{1}{39459}$ inch. The fact that it is possible to see these lines so clearly, although the spaces between them (which appear just a little thicker than the actual rulings) are only of the order of a half-wave-length of red light, is a particularly interesting physical fact. These exceedingly fine gratings of 40,000 lines to the inch are proving of great use in interferometric work, but for spectroscopic work are not serviceable, rulings of 14,000-20,000 to the inch being of maximum use, especially the celebrated 6-inch gratings ruled on a space of $5\frac{1}{2}$ inches by Prof. Rowland with 20,000 lines to the inch on a concave spherical surface of polished speculum metal of 21·5 feet radius of curvature. For all general spectroscopic purposes the Rowland gratings on speculum metal with 14,000 or 15,000 lines to the inch, or the Thorpe transparent replicas cast in

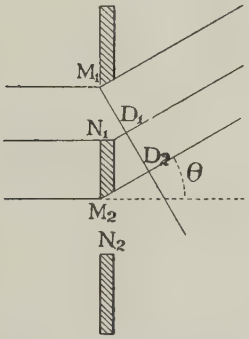


FIG. 607.—Normal Incidence.

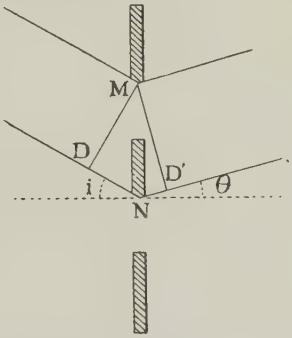


FIG. 608.—Oblique Incidence.

The two Modes of employing a Diffraction Grating.

celluloid and mounted on plane-parallel glass, are excellent. Zeeman, in his celebrated work on the doubling and tripling of the bright spectrum lines of incandescent vapours under the influence of the magnetic field, used a concave Rowland grating with 14,438 lines to the inch and a radius of curvature of ten feet (see page 785 for further practical details).

For projection purposes the rulings of Nobert, 3000 and 6000 to the inch (straight lines ruled with a diamond point on glass), or their photographic reproductions, and also the diffraction gratings of 3000 straight lines to the inch made specially for projection purposes by Messrs. Newton, afford excellent screen spectra. Messrs. Newton also make a very effective circular grating for projection, with 5488 circular lines to the inch.

There are two methods of using a grating, the **normal** method, and the method of **minimum deviation**. In the first the incident rays are caused to strike the grating normally, and in the second at an angle less than 90°, which is such that the deviation of the nth spectrum is a minimum, this being the case when the angles of incidence and diffraction are equal; for this angle the spectrum exhibits the clearest definition.

Considering first **normal incidence**, the conditions are represented in

Fig. 607, supposing the light to be incident from the left and to be diffracted towards the right, and the clear intervals a between the rulings to be approximately equal to the thickness b of the actual ruled opaque lines. If M_1 M_2 be successive first-element edges of two consecutive intervals M_1N_1, M_2N_2, and if $M_1D_1D_2$ be drawn perpendicular to the diffracted rays, θ being the angle of diffraction, then it will be obvious that the difference of path between the first element of the first aperture and the first element of the second aperture is M_2D_2. Now, if this be an even number of half-wave-lengths the light from the two sources (elements) will mutually reinforce, whereas if it be an odd number of half-wave-lengths there will be extinction if monochromatic light be employed or colour if white light be used. That is, as

$$\frac{M_2D_2}{a+b}=\sin\theta, \text{ or } M_2D_2=(a+b)\sin\theta,$$

for light reinforcement we have

$$M_2D_2=2n\,.\,\frac{\lambda}{2}, \text{ or } (a+b)\sin\theta=2n\,.\,\frac{\lambda}{2}=n\lambda.$$

If we replace $a+b$ by the single letter d, representing the distance between the ruled lines when each opaque line is imagined to be infinitely fine and the whole distance $a+b$ as the clear space between two consecutive ideally fine lines, we have, for maximum light transmission,

$$n\lambda=d\sin\theta.$$

It is interesting that this simple equation is similar to that which is proving so valuable in affording us the distance between successive planes of atoms, when a crystal is used as a three-dimensional grating for the diffraction of X-rays (see Chapter XXXIII.).

Obviously, also, from this equation, if we know the number of rulings (as we always do, the ruling machine recording it automatically), and hence d, and the order of the spectrum n, and if we measure the angle of diffraction θ, we have an exceedingly accurate method of determining the wave-length of light, provided that we use a grating in which the rulings are of a high degree of fineness and regularity and are adequate in number (as in the gratings with 14,000 lines to the inch). It will, of course, be clear that the equation refers to monochromatic light, the wave-length of which is λ. The angle of diffraction obviously increases with the wave-length λ, so that when white light is used the spectrum is produced instead of the single image of the source in the monochromatic light. The letter n represents the order, 1, 2, 3, etc., of this spectrum.

Considering now the case of **obliquely incident light,** that of minimum deviation, the conditions are represented in Fig. 608. The light now falls from the left on the grating at the angle of incidence i, and it is diffracted to the right at the angle θ.

The retardation δ is now $ND+ND^1$, and as

$$ND=(a+b)\sin i \text{ and } ND^1=(a+b)\sin\theta$$

we have

$$\delta = (a+b)\ (\sin i + \sin \theta).$$

The position of the nth spectrum is afforded, therefore, by the equation

$$(a+b)\ (\sin i + \sin \theta_n) = n\lambda,$$

or

$$n\lambda = d\ (\sin i + \sin \theta_n),$$

when we represent $a+b$ by the single letter d for the distance between the idealised lines.

The deviation for the nth spectrum is thus $i+\theta_n$, and this is a minimum when $i=\theta_n$, that is, when the deviation is $2i$. This obviously occurs when the angle of incidence is equal to that of diffraction. Hence, for the position of minimum deviation, that of equal angles of incidence and diffraction, we have

$$n\lambda = d \sin 2\theta.$$

The Colours of Mother-of-Pearl and Insects.—Intimately related to the play of colour which a fine grating displays by casual reflection, and to the similar colours often shown by the surfaces of finely laminated alternating-twin crystals, such as those referred to on pages 508 and 510, is the iridescence of mother-of-pearl, the carbonate of lime shells of the pearl-mussel *Meleagrina margaritifera* and other bivalves, the chief sources of which are the north-west coast of Australia, the Pacific Islands, and the East Indian Archipelago. It is this same mollusc, and especially a small variety of it, found near Shark's Bay, which produces the loose pearls which are so highly valued as gems. An investigation by A. H. Pfund [1] showed that mother-of-pearl owes its colours to two causes : (1) diffraction of light due to a grating-like structure of the terminal edges of successive laminæ of calcium carbonate, and (2) interference of light due to reflection from numerous parallel laminæ of sensibly equal thickness. It was found that the thickness of the laminæ in many different specimens lay between 0·4 and 0·6 of a micron (thousandth of a millimetre).

The exquisite iridescent colours exhibited by the wings, wing-scales, and wing-cases of many insects, especially of *Lepidoptera* (butterflies and moths) and *Coleoptera* (beetles), are also those of thin plates and diffraction gratings, due to similar structural causes —lamination, striation, and ribbed structures—rather than to pigments. Another cause is also the " metallic " reflection by a thin surface film. Occasionally also the scattering of light by small particles (as in the blue of the sky), the dispersion of light by prism-structures, and the combination of pigment colouring (especially green) with structural colours, are found to be further causes of these wonderful colours displayed by insects. For instance, the gorgeous males of *Ornithoptera poseidon* and *O. paradisea* are emerald green ; they exhibit a bright blue colour due to narrow plates of " chitin " separated by air-films, standing up at right angles to the surface of the wing-scale like rectangular teeth of a saw, but this blue is modified to green by a pigment resembling picric acid which dyes the chitin plates and the whole scale yellow. In other species of this

[1] *Frank. Inst. Journ.*, 1917, *183*, 453.

genus, *O. urvilliana* for example, the pigment is absent in parts, which appear therefore bright blue, the true colour due to the grating structure. There are also more obscure physical causes for the colours exhibited by other insects, which have not yet been satisfactorily explained, in spite of many distinguished investigators such as Michelson and R. W. Wood, and which afford a fascinating borderland study between Biology and Physics. An excellent account of researches on this subject of insect colouring is given by H. Onslow in *Nature*, 1920, *106*, 149, 181, and 215.

The Colours of Birds.—These are also due partly to pigments and partly to interference. In a communication to the Zoological Society on February 22, 1921, A. Mallock showed that an excellent discriminatory test is afforded by the application of pressure. If the colour alters when subjected to pressure it is a case of interference due to structure, but pressure does not appreciably affect the molecules of pigments. The greater part of the colours of feathers are shown by this test to be due to pigments, but the most brilliant are due to interference, such as those of humming-birds, ducks, and birds of paradise. The structure-layer causing the interference overlies a deep black substratum. The spacing of the structure is a multiple of the half-wave-length of the light which is reflected, and its regularity and order of dimensions are clearly revealed under a high power of the microscope.

CHAPTER XXXVIII

THE OPTICAL ELLIPSOID OF CRYSTALS AND DETERMINATION OF ITS CHARACTER

THE determination of the optical characters and constants of crystals becomes much simplified when the fundamental fact is remembered that the optical properties are represented in general by an ellipsoid, which may express either the relative velocity of the light vibrations transmitted in all directions through the crystal, or more simply the corresponding values of the refractive index. For the practical operations concerning the optical properties really resolve themselves into the location of, and measurement of the relative directional dimensions of, this ellipsoid.

In the cases of crystals belonging to the triclinic, monoclinic, and rhombic systems the ellipsoid is one of the most general form, with three unequal rectangular axes, as represented in light and shade in Fig. 609, the axes emerging at *a*, *b*, and *c*, *a* being the maximum axis, *c* the minimum, and *b* the intermediate axis. The three principal section planes are all ellipses. The difference shown in Fig. 609 between the axes *a* and *c* is very exaggerated, compared with what it usually is in the optical ellipsoids of crystals, which do not differ nearly so much from spheres (see Fig. 648, page 869). In a rhombic crystal the three axes are coincident in direction with the crystallographic axes, by reason of the symmetry In a monoclinic crystal only one is coincident with a crystallographic axis, the symmetry axis *b*, the other two rectangular axes lying in the symmetry plane, but anywhere in that plane ; and in a triclinic crystal the orientation of the ellipsoid has no necessary relation to the crystallographic axes whatever. In the cases of crystals belonging to the tetragonal, hexagonal, and trigonal systems the symmetry necessitates that two of the three rectangular axes of the ellipsoid are equal, converting it into one of rotation, the axis of rotation being identical in direction with the singular axis of tetragonal, hexagonal, or

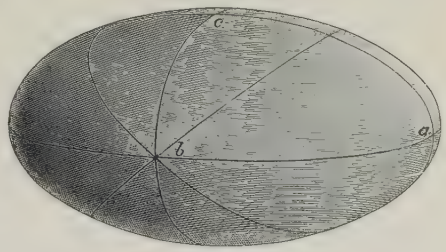


FIG. 609.—The Ellipsoid of General Form.

trigonal symmetry. In the cases, finally, of crystals belonging to the cubic system the perfection of symmetry causes all three axes of the ellipsoid to be equal, so that the ellipsoid becomes a sphere. Obviously the ellipsoid of revolution and the sphere are but special cases of the general ellipsoid, when first two and then all three of the unequal rectangular axes become equal.

Crystals possessing the symmetry of any of the five classes of the cubic system, therefore, exhibit similar optical properties in all directions within the crystal, just as if the crystal were so much glass, although this is a consequence of the perfect symmetry of the homogeneous structure, whereas in the case of glass the effect is due to the total lack of homogeneity in the mode of arrangement of the molecules, which renders the effect equal in all directions simply because it is the average effect in a solid which is merely a congealment of a highly viscous liquid, the molecules of which are restrained by their own friction from properly arranging themselves. In a cubic crystal, therefore, the refractive index is the same for all directions, so that there is no double refraction; also there is no "optic axis" or direction of unique single refraction (shortly to be fully explained, and quite distinct from any of the three axes of the optical ellipsoid, although its direction may coincide with that of one of them) developed, for there is only single refraction in every direction. Consequently no coloured rings and cross (uniaxial as explained below), or pair of lemniscate ring-systems and dark optic axial hyperbolic brushes (biaxial), are visible when plates of the crystal are examined in convergent polarised light. Cubic crystals are, therefore, said to be "isotropic."

Crystals endowed with the symmetry of any of the 19 classes of the hexagonal, tetragonal, and trigonal systems exhibit unique optical properties along the direction of the axis of revolution of the ellipsoid, that is, along the direction of their hexagonal, tetragonal, or trigonal main axis, the vertical crystallographic axis (except when the Millerian rhombohedral axes are used in the trigonal system, when the vertical axis of trigonal symmetry is not a crystallographic axis), while the optical properties are different in all other directions. The difference is at a maximum in all directions at right angles to the singular axis. The crystals are thus endowed with the property of double refraction. For **the refractive index [1] along the direction of the singular axis is either the greatest or the least exhibited by the crystal, the two possible types being termed respectively positive and negative.**

The refractive index along all the directions at right angles to the singular axis, that is, along all diameters of the circular section of the ellipsoid, is obviously the converse, being either the least or the greatest refraction which the crystal can show among all the infinite number of possible values corresponding to the various directions within the crystal.

[1] By "refractive index along" a direction is meant the refractive index corresponding to vibrations occurring along this direction, and not for the direction of propagation of the rays, which is at right angles thereto.

The refractive indices for any direction in the circular section, and for the principal axis at right angles to that section, are thus the two extreme values for the crystal, and the difference is the measure of the maximum double refraction. A ray of light transmitted along the principal axis, and the vibrations of which occur therefore in the circular section at right angles thereto, is said to be an "**ordinary**" ray, and the refractive index corresponding thereto is distinguished by the symbol ω. The other extreme refractive index is labelled ϵ, and corresponds to an "**extraordinary**" ray of extreme properties travelling in the circular section, and the vibrations of which occur parallel to the principal axis. Thus ω is the greater in negative crystals, while for positive crystals ϵ is the larger refractive index. The double refraction is consequently $\omega \sim \epsilon$; or it may be expressed always as $\epsilon - \omega$, the sign of the result then indicating that of the double refraction.

Also the crystal exhibits the phenomenon of an optic axis along the direction of the singular axis, the position of which is rendered visible, when a section-plate perpendicular to the axis is examined in the polariscope under crossed Nicols in convergent polarised light. For a rectangular black cross is observed of which the axis forms the centre, and around that centre are seen a series of circular concentric rings; the latter are spectrum-coloured when white light is employed but black when monochromatic light is used, and resemble Newton's rings. They are similarly derived by interference, but by the retardation of one set of rays behind the other instead of by difference in the lengths of the paths of the two sets. The crystals of the hexagonal, tetragonal, and trigonal systems are therefore said to be "**uniaxial.**" The reproduction of a photograph, taken by the author, of the interference figure afforded by such a plate of a typical uniaxial substance, calcite, is shown in Fig. 610, the Nicols of the polariscope being crossed for the production of the dark field.

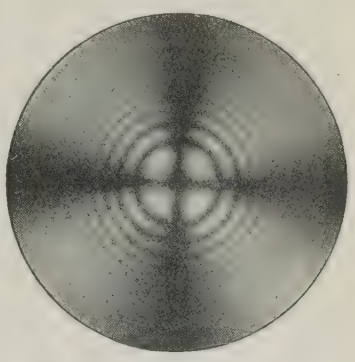


FIG. 610.—Uniaxial Interference Figure of Calcite.

Crystals exhibiting the symmetry of the 8 classes of the rhombic, monoclinic, and triclinic systems **have their optical properties represented by the general ellipsoid the three rectangular axes of which are of unequal lengths, the relative measure of which is afforded by the values of the refractive index along the three respective directions.** The measure is a direct one or a reciprocal one, according as we define the ellipsoid, the direct measure affording the "indicatrix" of Fletcher, and the polar reciprocal being the ellipsoid of Fresnel, both of which will be fully discussed and defined in Chapter XLI. The three values of the index corresponding to these three axial directions are generally labelled α, β, and γ.

It has been pointed out that in the case of the rhombic system the three axial directions of the ellipsoid are identical with the three crystallographic axes, by virtue of the symmetry. The relation of the lengths, however, is not necessarily similar.

In the case of the monoclinic system the direction of only one of the axes is coincident with a crystallographic axis, the symmetry axis b, the nature of the symmetry conferring the possibility of rotation to any extent about this axis. The ellipsoid may thus be so situated that its two other principal axes, while still at right angles to each other, lie anywhere in the symmetry plane, the exact position being definite for the same substance, but only at the same temperature and for the same wave-length of light. Indeed, it is usual for rotation actually to occur with change of wave-length, that is, as the crystal is illuminated with light of the different colours of the spectrum in succession, and also when the temperature is raised or lowered. Gypsum is a beautiful case of the change by temperature; the two rectangular maximum and minimum axes of the ellipsoid, while remaining inclined mutually at 90° in the symmetry plane, rotate together (with the ellipsoid) for 5° 41′ in that plane, about the symmetry axis, when the temperature is raised from 10° to 91° C., according to direct measurement by the author.

In the case of a triclinic crystal there is no rule or restriction whatever as to the orientation of the optical ellipsoid, which as far as the symmetry is concerned (centro-symmetry only at most) may have any possible situation with respect to the crystallographic axes.

A natural result of the general ellipsoid having three unequal axes and of the symmetry only controlling their directions and not their lengths, is that while one of them must be the maximum or longest axis and another the minimum or shortest, the third axis may be of any intermediate length, that is, it may approximate nearer to equality with either the maximum or the minimum axis. There are thus two possible kinds of these crystals, just as there are of uniaxial crystals, and they are similarly termed positive and negative. That variety which has the intermediate axis β (supposing the ellipsoid to be the expression of the refractive index) nearer in length to the minimum axis α is termed positive, and that in which the intermediate axis β approximates most to the maximum axis γ is termed the negative variety. Hence, taking the three refractive indices as expressive of the axial dimensions of the ellipsoid, the determination of these refractive indices for the three rectangular directions at once fixes the sign or type of the crystal; for when β works out to be nearer to α than to γ the crystal is positive, but when β is nearer to γ the crystal is negative.

If we consider next the principal section of the ellipsoid, that elliptic section the major and minor axes of which are the maximum and minimum axes of the whole ellipsoid, it will be obvious that there must be two diameters of this ellipse, somewhere between these longest and shortest diameters and symmetrically placed on each side of them, which are of equal length to the intermediate axis perpendicular to the section under consideration. Hence there are two sections of the ellipsoid which

are circular, each containing the intermediate axis and one of the two diameters in question. The directions perpendicular to these two circular sections will clearly be comparable to the singular axis, which is also the optic axis, of a uniaxial crystal; for the velocity of light vibration will be equal in all directions perpendicularly around it, while either greater or less along it. Hence in convergent polarised light the phenomenon of an optic axis, surrounded by a series of spectrum rings, but differing from a uniaxial interference figure in being traversed by only a single diametrical black bar instead of a rectangular cross, is observed through a plate cut perpendicularly to either of the two directions. Such an interference figure, afforded by gypsum, monoclinic hydrated sulphate of lime, $CaSO_4 . 2H_2O$, is shown in Fig. 611. If a plate be cut at right angles to that axis of the ellipsoid which is the bisectrix of the acute angle between the optic axial directions, both optic axes will be seen at once in the field of view of the polariscope, provided the angle of the lens system of the latter be wide enough to include them. The single bar again stretches across the field diametrically, passing through both axes, assuming that the plate is so arranged that this line joining the axes is parallel to either of the crossed Nicols; but it forms now one pair of arms of a black cross, the other pair of arms or cross-bar of which intersects it rectangularly midway between the two axes, and is usually much broader and less deeply black (see Fig. 612 next page). The inner rings soon give place to lemniscates like the figure 8 as the axes are receded from, and these in turn pass into outer ellipse-like lemniscates near the margin of the field. On rotating the section-plate, the black cross opens out into a pair of hyperbolic "brushes," the vertices of which are narrow and fairly well defined; each vertex passes through one of the optic axes, the position of which it thus precisely indicates, while the wings tail off into ever widening but diffusing streams on each side. For all practical purposes these brushes afford an excellent means of determining the apparent acute angle of the optic axes in air, and it will be shown later (Chapter XLVIII.) that by making the observation in a highly refractive liquid instead of in air, and making also a similar observation of the supplementary obtuse angle in the same liquid, by means of a second section-plate cut perpendicularly to the first plate and to that other axis of the ellipsoid which is the bisectrix of the obtuse angle in question between the optic axes, the true angle of inclination of the two optic axes within the crystal can be readily calculated with the aid of a very simple formula. The crystals of the rhombic, monoclinic, and triclinic systems are consequently termed **"biaxial."** The interference figure afforded by a typical biaxial substance, aragonite, the rhombic

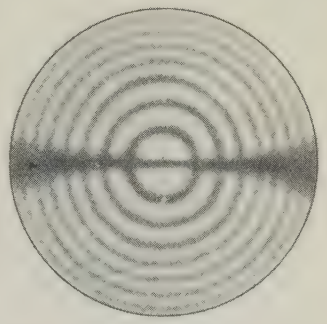


FIG. 611.—Interference Figure about one of the Optic Axes of Gypsum.

form of carbonate of lime, $CaCO_3$, in the dark field of the polariscope, with the Nicols crossed and parallel to the principal axial directions of the section-plate, which is cut perpendicularly to the acute bisectrix of the optic axial angle, is shown in Fig. 612; while Fig. 613 represents the appearance, when the section-plate (or the pair of Nicols simultaneously, actually the case for Fig. 613) is rotated 45° from this position, this arrangement being that which is practically employed in the measurement of the optic axial angle. Both figures are reproductions of the author's direct photographs.

The practical determination of the optical constants of crystals thus resolves itself into the following three main operations, which were briefly indicated in the introductory pages of Chapter XXXV., but which may now be more definitely expressed.

(1) The determination of the orientation of the optical ellipsoid, if this be not already fixed by the symmetry. As this latter is the case,

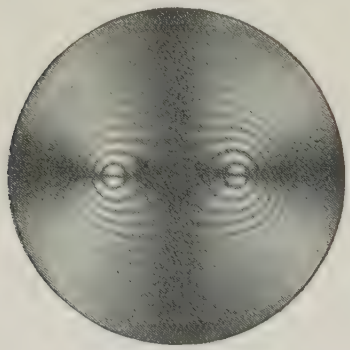


FIG. 612.

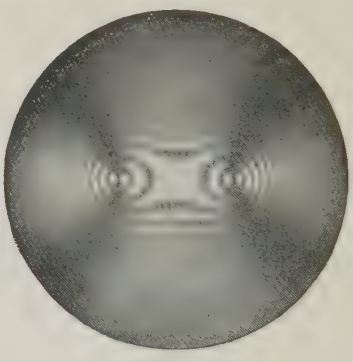


FIG. 613.

Biaxial Interference Figures of Aragonite.

however, for all but monoclinic and triclinic crystals, it is only when the symmetry of either of these two systems is developed that an experimental determination is necessary.

(2) The orientation of the ellipsoid being known, to determine the relative lengths of its three principal rectangular axes. This is achieved in practice by determining the three refractive indices, α, β, and γ, corresponding to these three directions of the rectangular principal axes of the optical ellipsoid, when the crystal is a biaxial one; or if the crystal be a uniaxial one, by determining the two refractive indices ϵ and ω, corresponding respectively to the principal axis of the ellipsoid of revolution and to directions perpendicular thereto. The difference between the two extreme indices, $\gamma - \alpha$, in the case of a biaxial crystal, or the difference of the two indices ϵ and ω in the event of the crystal being uniaxial, affords the measure of the amount of double refraction. In the latter case ϵ is greater than ω when the ellipsoid (indicatrix) represented by the refractive indices is vertically elongated like an egg, which is the case with positive uniaxial crystals, such as quartz, so that the

double refraction is then $\epsilon - \omega$; but ω is greater than ϵ for negative crystals such as calcite, the ellipsoid then being vertically compressed like an orange, so that the double refraction is $\omega - \epsilon$.

(3) In the case of a biaxial crystal the angle of separation of the two optic axes also requires to be determined, first of all the apparent angle in air, and secondly the true angle within the crystal. For the optic axial angle is a very characteristic property of any biaxially crystalline substance, and the nature of the dispersion of the axes of the ellipsoid for different colours of light, in the cases of monoclinic and triclinic substances, is often also of such a specific character as to enable the substance to be identified by means of it.

In all cases in which the position of the optical ellipsoid is not fixed by the symmetry, the orientation requires to be determined for light of a graduated series of different wave-lengths, at suitable intervals throughout the whole spectrum; for the position differs, as has just been indicated, for different colours of light. Determinations in ordinary white light are inadequate, although a crystal is always first explored in white light, before proceeding to use monochromatic light, and any preliminary adjustments are also carried out in white light. Both the refractive index and the optic axial angle must imperatively be determined in monochromatic light of the same graduated series of convenient wave-lengths, so that it is essential to possess a ready means of procuring monochromatic light, and of supplying it directly to the observing instruments. Such an apparatus for producing light of any desired wave-length will be described in Chapter XLIV.; it is one which has proved of inestimable service to the author in all his crystallographic researches.

For the purpose of carrying out the three operations above specified, which are the fundamental essentials of every crystallographic optical investigation, certain parallel-faced section-plates and 60°-prisms are required to be cut or ground (or both) out of the crystal, each having two truly plane polished surfaces, accurately orientated with respect to the optical ellipsoid. It is the difficulty presented by the problem of preparing these plates and prisms that has so seriously hindered in the past the investigation of the optical properties of crystals, but an instrument for carrying out this all-important part of the work, the cutting-and-grinding goniometer, has been devised by the author, which accomplishes the task with the minimum of trouble and the maximum of accuracy and perfection, rendering, indeed, what was formerly the most difficult part of a crystallographic research at the same time comparatively easy and very interesting. It will be described in Chapter XLIII.

CHAPTER XXXIX

THE TRANSMISSION OF LIGHT THROUGH UNIAXIAL CRYSTALS

It has been shown in the last chapter that the sign of the double refraction of a uniaxial crystal is negative when $\omega > \epsilon$, and positive if $\epsilon > \omega$. Hence, the velocity of vibration being inversely as the refractive index, the extraordinary ray moves with the greatest velocity in negative crystals, while the ordinary ray is the quicker in positive crystals.

Quartz, SiO_2, and calcite, $CaCO_3$, are two typical examples of positive and negative uniaxial crystals respectively, and their pairs of refractive indices for sodium light, and the amounts of their double refraction, are the following :

For quartz (positive) $\omega = 1{\cdot}5443$, $\epsilon = 1{\cdot}5534$; $\epsilon - \omega = 0{\cdot}0091$
,, calcite (negative) $\omega = 1{\cdot}6583$, $\epsilon = 1{\cdot}4864$; $\omega - \epsilon = 0{\cdot}1719$.

Both these colourless transparent minerals are of great use in crystallographic optics.

When a beam of parallel rays is allowed to pass through a rhomb of calcite normally to one of the pairs of parallel faces, as in Fig. 614, or in any other direction than the principal axis, it separates into two rays on entering the crystal. One, termed **the ordinary ray,** behaves as if the crystal were cubic, or a piece of glass, and leaves the crystal parallel to its original direction, indeed in the same straight line when the incidence is strictly normal. The other, conventionally known as **the extraordinary ray,** is refracted to one side in any case, and emerges laterally displaced, but of course parallel to the original path as the two faces of the rhomb through which it passes are strictly parallel, being either natural or cleavage faces, each inclined 74° 56′ to the other pair of faces. The extraordinary ray does not obey the law of sines, except when the plane of incidence is perpendicular to the principal axis, and therefore a circular section of the optical ellipsoid of revolution.

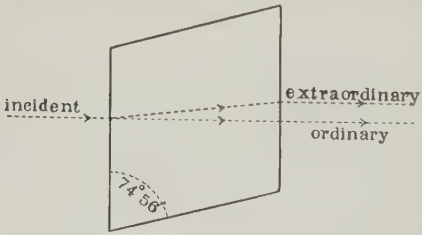


Fig. 614.—Passage of Light through Rhomb of Calcite.

When the rhomb is rotated about the direction of the incident ray, the two parallel faces through which the ray passes being thus turned in their own plane, the extraordinary ray rotates round the ordinary one. This may be well shown by focussing on the screen, by means of a projection lens, the image of a round aperture in a metal plate placed in front of the lantern condenser. The arrangement shown later in Fig. 636 (page 858), in connection with another experiment, consisting of four apertures in a rotatable diaphragm, is a very suitable one, enabling such an aperture to be chosen as is of most convenient size ; the lens on its adjustable stand is also shown in the figure. On interposing the calcite rhomb in the path of the rays, either between the aperture and the lens or after leaving the lens, preferably at their crossing-point where the beam is narrowest, two images are seen on the screen, and if the rhomb be mounted for rotation (like the double-image prism seen to the extreme right nearest the screen in Fig. 636) one image, that produced by the ordinary ray, will be observed to remain stationary if the incidence be normal, while the other image due to the extraordinary ray rotates round the fixed one, on rotating the rhomb. When such a rotating rhomb on adjustable stand is used, the whole apparatus is precisely as shown in Fig. 636 without the large Nicol prism.

If, instead of a natural rhomb, a 60°-prism of calcite be employed, and a rectilinear slit instead of a round aperture in front of the lantern, two spectra are afforded on the screen, both rays being now refracted to one side as with a spectroscopic prism of glass, but one ray, the ordinary, at a much more considerable angle of deviation than the other, the extraordinary, corresponding to its much higher refractive index.

The experiment is shown in Fig. 615. The electric lantern is to the left, with a water cell 2 inches thick in front of the 4½-inch condenser, the cell being readily attachable on a short tubular fitting also 4½ inches in diameter, to the lantern front. The ordinary projecting lens and the carrier bar on which it is adjustable by rack and pinion (shown in Fig. 638, page 860) are entirely removed, the bar simply unscrewing from a boss in the lantern front ; an additional support for it is the little stirrup column standing up from the water-cell fitting.

The slit is carried in front of the water cell, and in the experiment as performed by the author a disc 6 inches in diameter is employed having a fixed permanent slit 2 inches long and an eighth of an inch wide cut in it, and two vertical bevelled jaws in front sliding in horizontal dovetails so as to be able to vary the width of the opening ; there are also two similar horizontal jaws behind, adjustable in vertical dovetails, which enable the length of the slit to be varied. The disc is mounted on a standard which is adjustable for height, and the base of which is also provided with a lateral adjustment in a dovetailed bed, which rests in turn on a laterally elongated mahogany base, one of a series of sliders in a mahogany grooved and rabbeted bed, forming the optical bench of the large projection polariscope. At 4, 5, or 6 inches distance comes a similarly mounted projection lens of 2½ inches diameter, and either 4, 5, or 6 inches focus. Next is a large Nicol prism to be described in the next chapter, and then the calcite prism, mounted on a little circular table carried on a similar adjustable standard to those bearing the slit and the lens.

The amount of separation of the two spectra depends on the direction in which the prism is cut, and of the two refractive indices, corresponding

to the positions of the two images when the prism is adjusted for minimum deviation, one always has the value 1·6583, namely, that belonging to the ordinary ray; while the other has a value which may vary from 1·4864 to 1·6583, the latter occurring when the separation of the two rays has become zero, that is, when no double refraction occurs, which only happens when the prism is so cut that the ray travels along the optic axis.

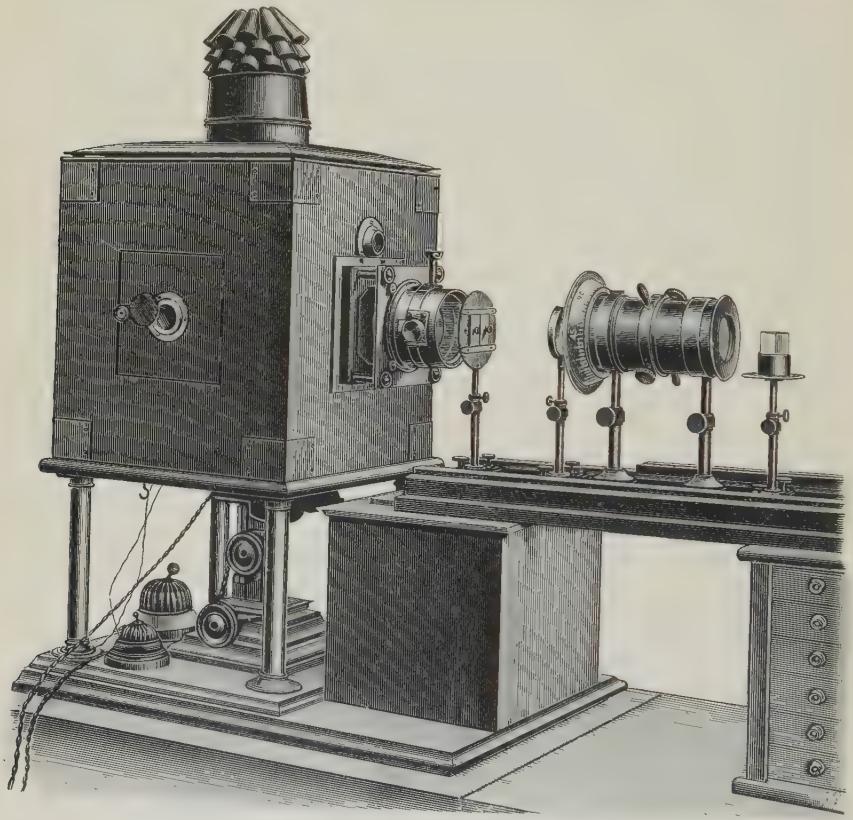


FIG. 615.—Experiment demonstrating Rectangular Polarisation of the two Spectra afforded by Calcite Prism.

This latter case of a 60°-prism of calcite cut to afford only one spectrum, when arranged for minimum deviation, as if it were a prism of glass, is one much employed in optics for spectroscopic purposes. The refracting edge is made perpendicular to the trigonal axis (the optic axis), and the third basal face of the prism (opposite to the refracting edge) parallel both to this edge and to the axis as shown in Fig. 616. When arranged at minimum deviation for any one colour—the incident and refracted light rays of that wave-length being then equally inclined to the base — the direction of transmission within the crystal-prism is

parallel to the base, along the optic-trigonal axis, and the vibrations thus occur entirely in the circular section of the ellipsoid perpendicular thereto, with equal velocity in all azimuths, corresponding to $\omega = 1{\cdot}6583$.

The condition for extreme separation of the two images is afforded when the prism is cut in either of two ways, both of which ensure that one ray vibrates parallel to the axis, while the other vibrates perpendicularly to it. The first mode of cutting is shown in Fig. 617, and the only condition is that the refracting edge shall be parallel to the axis, the prism being orientated anyhow around that axis. Whatever be the orientation, a beam of monochromatic light entering at minimum deviation is transmitted through the crystal perpendicularly to the axis, and is separated by the crystal into two distinct rays, composed of two sets of vibrations, both occurring at right angles to its path, one set

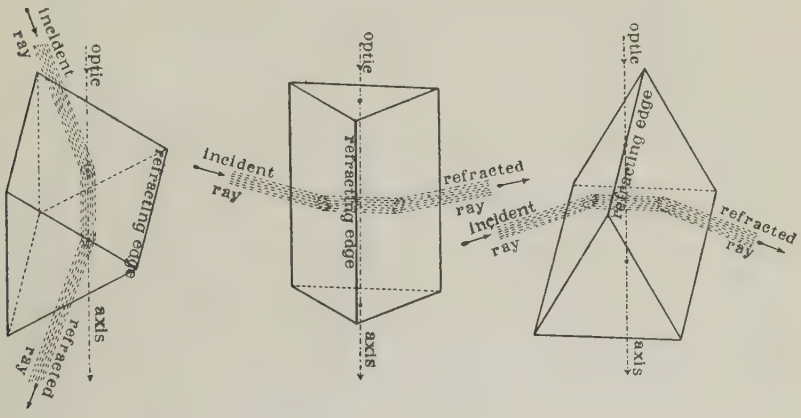


FIG. 616. FIG. 617. FIG. 618.

The three Modes of cutting a 60°-Prism of a Uniaxial Crystal.

vibrating in the circular section perpendicular to the axis, and the other set vibrating parallel to the axis. Obviously, therefore, there will be two images of the slit afforded, corresponding respectively to $\omega = 1{\cdot}6583$ (as always for a ray vibrating in the circular section), and to $\epsilon = 1{\cdot}4864$ (that formed by rays vibrating parallel to the axis).

The second mode of cutting the prism is so that the refracting edge is perpendicular to the principal axis, and also so that the axis bisects the refracting angle, as shown in Fig. 618. In this case the monochromatic beam traverses the crystal-prism at minimum deviation in the circular section perpendicular to the axis, and the two rays into which it divides vibrate parallel and perpendicular (in the circular section) to the axis respectively, the former corresponding to $\epsilon = 1{\cdot}4864$ and the latter to $\omega = 1{\cdot}6583$.

The images of the slit in monochromatic light, or the spectra in white light, are thus separated at the maximum possible distance for calcite by these two latter prisms, so that, as we shall see when we come to the practical determination of refractive index in Chapter XLVI., such prisms each

afford the two indices ω and ϵ directly. Moreover, the images are formed by rectangularly plane-polarised light, one image extinguishing when a Nicol prism introduced in the path of the rays is arranged at its 0° position, and the other disappearing when the Nicol is set at 90°, the former being that produced by light vibrating parallel to the refracting edge of the crystal-prism. In the case of the prism represented in Fig. 616, the unique image never extinguishes at all, for any position of the Nicol, the prism behaving in this respect also as if the crystal were singly refractive.

The Nicol is shown in position in Fig. 615 for demonstrating these facts, the 60°-prism actually used being of the type shown in Fig. 617, its refracting edge being parallel to the optic axis.

These phenomena with calcite are typical of uniaxial crystals in general, and the three above described modes of cutting 60°-prisms are equally applicable to any uniaxial substance. The values of the indices, the corresponding amounts of separation of the images, and the dispersion of each spectrum in the cases of the two latter prisms (Figs. 617 and 618), as well as the order of the values corresponding to positive or negative character, will vary for different substances, but the principles are the same.

Thus, **in uniaxial crystals the ordinary ray always vibrates perpendicularly to the axis** (along a direction parallel to a diameter of the circular section) **and with the same velocity ; it is consequently transmitted equally in all directions, and has a spherical wave-surface.** Its refractive index ω is the maximum index in the case of calcite (1·6583) and all other negative uniaxial crystals, but the minimum index in the case of quartz (1·5443) and all other positive uniaxial crystals. Its velocity is the converse, namely, the minimum for a negative crystal and the maximum for a positive one.

On the other hand, **the extraordinary ray is unequally transmitted in different directions, other than those lying in the circular section, and its wave-surface is thus an ellipsoid of revolution.** In negative crystals such as calcite, the velocity of transmission becomes greater, and the refractive index conversely less, as the direction of the principal axis is left and that of the circular section approached, until for directions lying in the latter the maximum velocity and minimum index is reached. Thus **the extraordinary ray in the case of calcite (negative) has its minimum refractive index 1·4864 when transmitted perpendicularly to the axis, its vibrations being parallel to the axis ;** and it has its maximum index 1·6583, equal to the ordinary, when it travels along the axis, its vibrations being perpendicular thereto. Hence vibrations parallel to the axis always afford the index 1·4864, and vibrations perpendicular to the axis yield 1·6583 as the numerical value of the index. The opposite is true of quartz (positive), the velocity diminishing and the refractive index increasing up to a maximum of 1·5534, as the direction of transmission recedes more and more from the principal axis until it finally becomes perpendicular to that axis.

The forms of the wave-surfaces of the ordinary and extraordinary

rays of a negative uniaxial crystal are represented in vertical section in Fig. 619, and those of a positive crystal in Fig. 620. It will be observed that in the former case the circle representing the wave-surface of the ordinary ray is inside the elliptic section of the extraordinary wave-

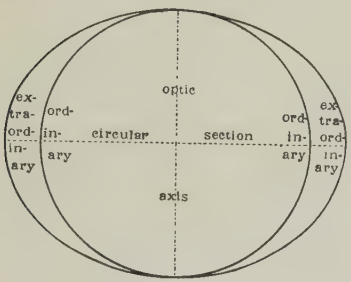


FIG. 619.
Negative Uniaxial Wave-surfaces.

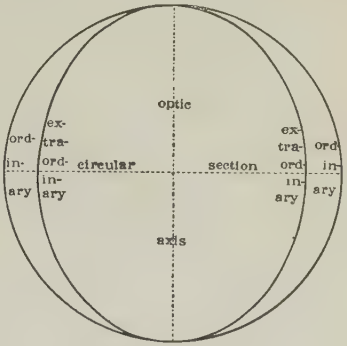


FIG. 620.
Positive Uniaxial Wave-surfaces.

surface, giving the whole figure a flattened shape; while in the latter case the circle is outside.

If we draw the ellipsoids of revolution representing graphically the refractive indices, for a negative and a positive crystal respectively, we obtain an oblate spheroid in the former case, and one standing up like an egg in the latter case, as shown likewise in vertical section in Figs. 621

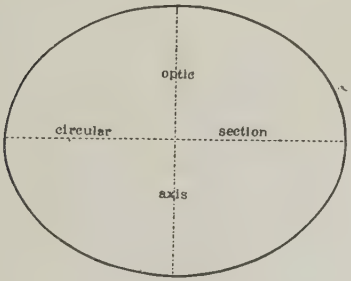


FIG. 621.
Negative Indicatrix.

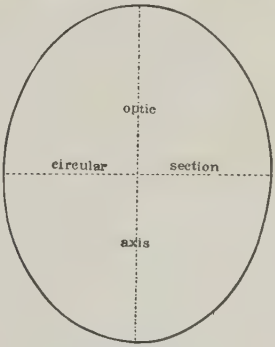


FIG. 622.
Positive Indicatrix.

and 622. Such an ellipsoid of refractive index is the "indicatrix" of Fletcher, which will be discussed more fully in connection with biaxial crystals in the next chapter.

In each of the cases represented in Figs. 621 and 622 the indicatrix resembles the extraordinary wave-surface.

For the determination of the shape of the wave-surface it is necessary to measure the two velocities of propagation of the extraordinary ray,

when it travels respectively parallel and perpendicular to the axis of the crystal. For the ratio of these quantities is that of the two axes of the ellipse which generates the wave-surface ellipsoid of revolution. As the former velocity is identical with that of the ordinary ray, the ratio in question is : $V_{\text{ordinary}} : V_{\text{extraordinary}}$, that is, the inverse ratio of the two refractive indices ω and ϵ. Hence, we have only **to measure the refractive index of the ordinary ray for any direction, and that of the extraordinary ray at its greatest difference from the ordinary when propagated perpendicularly to the optic axis and, therefore, vibrating parallel to the axis.** For it must be clearly remembered that the refractive index corresponds to the vibration direction, not to the direction of propagation of the ray. Thus the whole matter resolves itself experimentally into **the determination of the refractive index ω for light vibrations perpendicular to the axis, and of the index ϵ for vibrations parallel to the axis.**

This we have seen can be achieved by the use of a single 60°-prism cut according to the method of either Fig. 617 or 618. In the case of the prism represented in Fig. 617, when set for minimum deviation, one of the two rays into which the beam separates on entering the crystal vibrates parallel to the prism-edge and therefore to the axis, and thus affords ϵ ; the other vibrates perpendicularly to the axis and to the prism-edge, and consequently affords ω. A Nicol before the eyepiece of the goniometer-spectrometer, when arranged at 90° (assuming the divided circle itself to move with the Nicol and the vernier zero or indicating mark to be fixed at the top of the vertical diameter), that is, with its plane of polarisation (parallel to the 0°-180° diameter of its divided circle) horizontal and its vibration direction (parallel to the 90°-270° diameter of the circle) therefore vertical, lets through only the ray vibrating vertically, parallel to the edge of the prism and to the axis, thus only permitting the ϵ-image of the slit to be visible ; while at 0° (plane of polarisation vertical and vibration direction horizontal) the Nicol lets through only the other rays vibrating horizontally, perpendicularly to the axis and prism-edge, thus isolating the ω-image. In the case of the prism shown in Fig. 618, the image seen when the Nicol is at 90° (vibrations, as always for 90°, parallel to the refracting edge) corresponds to and affords ω, while that visible when the Nicol is at 0° gives ϵ. At the 45° position of the Nicol in the case of either prism both images are seen, but with only their partial intensities. Their angular separation when arranged for minimum deviation depends, of course, on the amount of the double refraction.

The Nicol of the spectrometer-goniometer No. 1*a* of Fuess, which the author always employs for refractive index determinations, is arranged to move with the vernier, the circle being fixed ; the Nicol is mounted so that the plane of polarisation is parallel to the diameter passing through the zero graduation of the vernier at the end of the radial arm, which moves with the Nicol ; the fixed circle about which the arm with its vernier and the Nicol rotates has its 0°-180° diameter vertical, the zero at the top, the 90°-270° diameter being horizontal,

with the 90° mark at the right. Hence, when the Nicol is arranged so that the arm is horizontal with the zero mark of the vernier opposite the 90° graduation, the vibration direction of the Nicol is vertical, and thus parallel to vibrations of light in the crystal which are parallel to the refracting edge of the crystal prism. The image of the slit which is then transmitted is due therefore to such vibrations only, the image corresponding to horizontal vibrations perpendicular to these being completely extinguished. When the vernier arm is rotated upwards till its zero mark is opposite the 0° graduation, the vibration direction is horizontal. The use of such a Nicol in front of the eyepiece of the spectrometer telescope is invaluable in enabling us not only to isolate the image corresponding to either direction of vibration, for measurement purposes, but also to determine the direction of vibration of the light composing any image.

The determination of both refractive indices ω and ϵ at once may also be achieved by employing the principle of total reflection. For any plate of a uniaxial crystal other than one perpendicular to the axis exhibits two limits of total reflection, corresponding to the ordinary and extraordinary rays. The value of the former is always the same, namely ω, which can thus be got from a plate of any orientation ; but the extreme value of the latter is only afforded by the second limit when the plate is parallel to a principal section, that is, to the axis, two rectangular diameters in it then corresponding to the axis and its perpendicular.

Résumé.

Rays travelling along the optic axis (principal axis) of a uniaxial crystal afford only one refractive index, ω, corresponding to vibrations in the circular section of the optical ellipsoid of revolution. Any ray passing obliquely through the crystal and its ellipsoid is resolved into two components. One component is plane-polarised in the principal section (that containing both the direction of the ray and the optic axis) and vibrates perpendicularly thereto along a diameter of the circular section ; whatever be the direction of the ray this component, which is conventionally termed the ordinary ray, consequently always gives the same index of refraction, which is symbolised by ω. The other component is an extraordinary ray, and its vibration direction and refractive index differ with the direction of the ray. The difference in refractive index from that of the ordinary ray is most accentuated when the ray is transmitted in the circular section itself perpendicular to the singular axis, its vibrations being then parallel to the axis ; and this extreme value for the second refractive index is characteristic of the extraordinary ray and is labelled ϵ.

Hence, the principal practical task connected with the optical properties of uniaxial crystals is to determine the two extreme refractive indices ω and ϵ. Their difference is the measure of the double refraction.

Thus in general, in all uniaxial crystals any ray is divided into

(1) An ordinary ray, of which the vibrations are always perpendicular to the axis, and perpendicular to a principal section and to the direction of the ray, and of which the plane of polarisation is a principal section. The wave-front is also perpendicular to the direction of the ray, the wave-surface being a sphere.

(2) An extraordinary ray, polarised in the plane perpendicular to a principal section and parallel to the ray itself, and of which the vibrations occur in a principal section and perpendicular to the ray, and hence parallel to the axis in the special case when the ray is directed along the circular section perpendicular to the axis. This special case is always used for the determination of the refractive indices by a 60°-prism cut as in Fig. 617 or 618. The wave-front is also perpendicular to the direction of the ray in this special case, and also when the ray is propagated along the axis, but generally, for all other directions, it is slightly inclined to the direction of the ray, the wave-surface being an ellipsoid of revolution and not a sphere, as in the case of the ordinary ray.

In a positive uniaxial crystal the ordinary refractive index ω (vibrations perpendicular to axis) is the minimum, and the extraordinary refractive index ϵ (vibrations parallel to axis) the maximum. Example, quartz, SiO_2, $\omega_{Na}=1{\cdot}5443$, $\epsilon_{Na}=1{\cdot}5534$.

In a negative uniaxial crystal the ordinary refractive index ω (vibrations also perpendicular to axis) is the maximum, and the extraordinary refractive index ϵ (vibrations also parallel to axis) is the minimum. Example, calcite, $CaCO_3$, $\omega_{Na}=1{\cdot}6583$, $\epsilon_{Na}=1{\cdot}4864$.

CHAPTER XL

CALCITE POLARISING AND DOUBLE-IMAGE PRISMS

It will be convenient at this stage, after having discussed in detail the passage of light through calcite, as a type of a uniaxial crystal, to describe the construction of the polarising prism devised by Nicol [1] in the year 1828, especially as its use has been so markedly demonstrated in the last few pages.

The Nicol Prism.—This prism of the beautifully perfect form of calcite, carbonate of lime, $CaCO_3$, known as "Iceland spar," affords us the most satisfactory means yet discovered of producing a beam of plane-polarised light. Its importance in crystallographic optics is simply incalculable, owing to the absolute transparency and freedom from colour of Iceland spar, and the perfection of the polarisation. Moreover, the "Nicol," as it has come to be familiarly called, is as effective an analyser as it is a polariser, and the dark field obtained with a well-constructed pair of Nicols is practically a perfect extinction of light, and the images of objects polarised suffer no distortion.

To construct a Nicol prism a clear flawless cleavage rhombohedron of calcite, about three times as long as broad, is selected, such as is shown in Fig. 623. It is carefully cut in two halves along a diagonal plane, APCQ in Fig. 623 and Fig. 624, and AC in Fig. 625. The two cut surfaces are polished truly plane, great skill being required on account of the softness of calcite, and cemented together again, in the same position as before cutting, with Canada balsam. The exact direction of the plane of section is a matter of importance. It is parallel to the longer diagonals HE and GF of the end-faces (assuming the four long faces equally developed), almost joins two opposite corners A and C of the rhombohedron, and makes an angle BAC (Fig. 625) of 22° with the long edge of the rhomb AB or CD. The section-plane is also perpendicular to the principal section BAA′ (Fig. 623), BA being a long edge and AA′ the direction of the optic axis of the crystal; that is, the section-plane is perpendicular to the plane containing both the long edge AB and the

[1] *Edinburgh New Phil. Journ.*, 1828, *6*, 83; 1839, *27*, 332. William Nicol (1766–1851) was a teacher of Physics in Edinburgh; he was a remarkably skilled practical worker in optics, and constructed many prisms with his own hands. He was elected a Fellow of the Royal Society of Edinburgh in 1838.

shorter diagonal AD of the end-face, as well as the optic axis, which is also the vertical trigonal crystallographic axis.

The natural cleavage end-faces are nearly but not quite also perpendicular to the section-plane, the exact angle being 87° 7′. For the edge AB (or the strip-face $e=(101)$ which often symmetrically replaces this edge on calcite) is inclined 70° 53′ to the natural end-face $r=(010)$ of the rhombohedron (see table of angles of calcite at end of Chapter XXIII.); as the section-plane is inclined 22° to the edge AB, these two angles, together forming the supplement of the angle in question between the section and the end-face, make up 92° 53′, so that the supplementary angle under discussion is 87° 7′. It is made 90°, therefore, by grinding away 2° 53′ in the proper direction (thickest part removed at corner A). Indeed the operations are

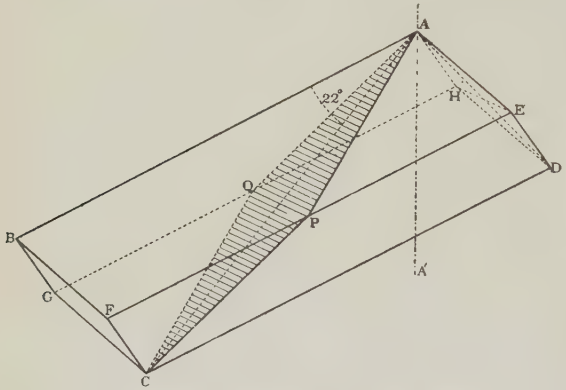


FIG. 623.—Construction of the Nicol Prism.

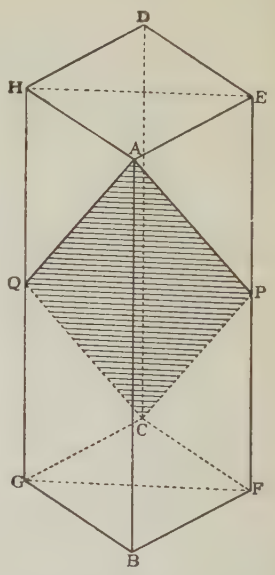


FIG. 624.—Nicol Prism vertically arranged to show another View of the Section-plane.

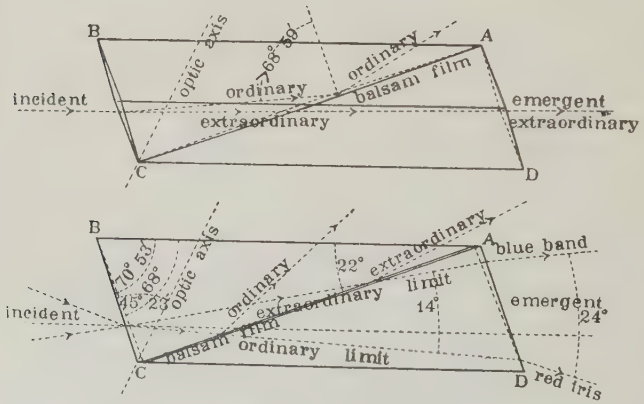


FIG. 625.—The Passage of Light through a Nicol Prism.

conveniently carried out by first making the ends to have the required inclination of 68° to the edges AB and CD, and then cutting the crystal through at right angles to these ends diagonally from A to C (Fig. 625).

We have seen that the two refractive indices of calcite for sodium light are $\omega = 1{\cdot}6583$ (ordinary ray) and $\epsilon = 1{\cdot}4864$ (extraordinary ray). The refractive index of Canada balsam for sodium light is intermediate between these, namely, 1·548.[1]

Now the index of refraction of the ordinary ray of calcite as compared with balsam is obviously $\frac{1{\cdot}6583}{1{\cdot}548} = 1{\cdot}0712$. If we calculate the corresponding critical angle ϕ for the passage of light from balsam to the denser calcite (as regards the ordinary ray), by finding the angle the sine of which is equal to the reciprocal of this index (see Chapter XXXVII., page 811), we have :

$$\sin \phi = \frac{1}{1{\cdot}0712}, \text{ and } \phi = 68° \, 59'.$$

When the incident light enters the Nicol prism at the end-face BC (Fig. 625, upper figure) it is separated into an ordinary and an extraordinary ray, as usual for a uniaxial doubly refractive crystal, both of which rays are bent by refraction as the incidence is not normal, and the ordinary more than the extraordinary ray, corresponding to its higher refractive index. The variable index of the extraordinary ray (the ordinary always being 1·6583 but the extraordinary varying from this down to 1·4864) is about 1·54 for the particular direction which it takes through the prism, practically the same as that of the balsam, through which, therefore, it is readily transmitted. On the other hand the ordinary ray, always possessing the index 1·6583 in calcite whatever the direction, arrives much more bent at the balsam layer, which it strikes at an angle of incidence (measured from the normal to the layer) greater than the critical angle 68° 59′ just calculated. It is consequently reflected totally to the side of the prism, where it is absorbed by dull lamp-black with which the cork mount is painted. Cork is always used as the mount for calcite prisms on account of the relative softness of the crystal and the general convenience of cork from every point of view. The interior of the cork mount is cut to the shape of the rhomb, and its exterior shape is cylindrical ; it is subsequently mounted immovably with cement in a metal tubular mount, which is in turn capable of rotation within an outer brass or gun-metal tube. The rotation is usually indicated on a silver divided circle, either attached to the outer tube or carried by the inner tube as a projecting bevelled flange, and thus moving with the prism itself and its inner metallic and cork mounts ; a silver vernier or indicating mark is carried by the other tube. The mode of mounting will be clear from Figs. 636 and 637 (pages 858 and 859), the latter of which shows on the left one of the pair of large

[1] This is the mean of the values given by Preston (*Theory of Light*, p. 320) and by Schaller and Calkins (taking their highest value) (*Amer. Journ. Sci.*, 1910, *29*, 324). See table, page 809.

Nicol prisms of $2\frac{1}{2}$ inches clear minimum aperture, belonging to the author's projection polariscope. Both these large prisms, arranged as a projection polariscope for parallel light, are shown in Fig. 633, page 853, and one of them also in use in Fig. 636 in an experiment described later in this chapter.

The only light which leaves the Nicol prism is thus that of the extraordinary ray, the vibrations of which are parallel to the principal section, the plane containing AB, the axis AA′ (Fig. 623), and the shorter diagonal AD of the end-face, that is, the plane of the paper in Fig. 625. The plane of polarisation is, according to the usual convention, perpendicular to this, namely, perpendicular to the plane of the drawing in Fig. 625. The direction of the emergent ray is parallel to that of the incident ray, but a little laterally displaced. The incident ray must not be inclined more than 14° 29′ to the axis of the Nicol, on the side of the acute corner B, in order that total reflection of the ordinary ray shall occur.

On looking through a Nicol prism at an illuminated surface, such as a white wall-screen or a white cloud in the sky, the limitation of the angle of usefulness will be perceived to be somewhere between 15° and 20°. There are two more or less clearly marked somewhat curved boundaries. One is a blue band beyond which the field is dark; this marks the limit where the extraordinary ray also becomes totally reflected at the balsam film. The other limit is the commencement of a series of spectrum-coloured interference fringes, merging eventually into a region of greater brightness; the first interference band marks the limit beyond which the ordinary ray is no longer eliminated by total reflection, and the bright region is that of no apparent polarisation, where both ordinary and extraordinary rays are transmitted. The blue band limit of the extraordinary ray begins to be formed when the incident light is so inclined to the axis of the Nicol that the extraordinary ray strikes the balsam film at an inclination of 7°-10°. These facts will be rendered clear with the aid of the lower diagram in Fig. 625.

The angular width of the polarised field within the prism is about 14°, which corresponds to a useful field of about 24° in the external air.

The optic axis makes an angle of 45° 23′ with the natural end of the rhomb BC or AD, which brings the axis 44° 37′ − 2° 53′ = 41° 44′ from the section-plane. The bisecting line of the internal angle is not parallel to the long edges of the rhomb, hence the origin of the practice of trimming the ends 2° 53′ in the direction which partially corrects this obliquity. The two long edges AB and CD are also often trimmed to the same extent, so that the joint effect is to bring the axis of the Nicol considerably nearer to the bisecting line.

Many variations on the prism of Nicol have from time to time been made, some of which will be referred to directly. In the author's experience, however, none are to be preferred to the original plan of Nicol, when carried out by a master hand such as we have fortunately possessed in England in the late Mr. C.D. Ahrens (who died early in the year 1918),[1] who has constructed, as far as the author is aware, all the large Nicols

[1] See *Journal of the Queckett Club* for June 1918.

in this country. Such large prisms can now no longer be made, the original magnificent deposit of enormous clear rhombs of Iceland spar at Eskifjördhr (see page 344) having become exhausted. Such as exist are consequently very valuable. The two described later in this chapter in connection with the author's projection polariscope (Fig. 633, page 853) have a clear aperture of $2\frac{1}{2}$ to 3 inches, and are one of the few original pairs made by Mr. Ahrens. Perhaps the most celebrated of these original pairs of Nicols are those of even larger aperture constructed for the late Mr. Spottiswoode

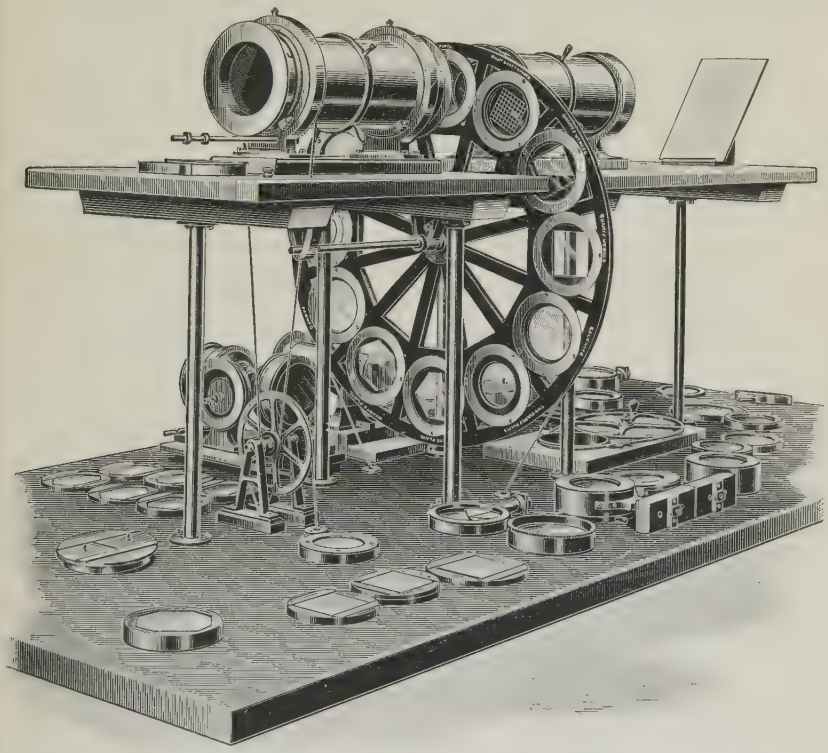


FIG. 626.—Large Nicol Prism Polariscope by Ahrens in the Science Museum at South Kensington.

and now in the Royal Institution. Another magnificent pair, of the same large size, nearly 4 inches clear circular aperture, have been acquired for the nation, the author having had the good fortune to assist in their acquisition; they are now in the Science Museum at South Kensington, where they are mounted, as shown in Fig. 626, as a horizontal table polariscope. The nearest prism, the analyser, can be rotated from outside the large protective glass case in which they are enclosed, and each of a fine collection of quartzes and other polarising objects which accompanied them, mounted on a large rotating wheel, can be brought in turn as desired between the polariser and analyser by manipulation of a second large milled

head outside the case. The Royal Institution possesses a second pair of Nicols, $2\frac{5}{8}$ inches aperture, formerly also belonging to Mr. Spottiswoode; and also the two somewhat larger historic Nicols of Prof. Tyndall, besides a single very large Nicol formerly belonging to Mr. De la Rue.

There is, happily, plenty of smaller calc-spar constantly being discovered, so that Nicol prisms for all ordinary crystallographic apparatus and the polarising microscope are more or less readily procured, and form the most efficient of polarisers and analysers.

As calcite is a soft mineral, hardness only 3 (see Chapter XXIX.), the polished ends of a Nicol prism should never be touched for cleaning purposes with anything but the softest camel-hair brush, and only in the last resort gently rubbed with the very softest of chamois leather. Large Nicols should always be put away with the section-plane vertical, as otherwise thin-film colours are apt to develop in the balsam film.

Trimmed and Flat-ended Nicols.—Some of the more recent Nicols constructed by Mr. Ahrens have been trimmed the other way, the end-faces being made to be

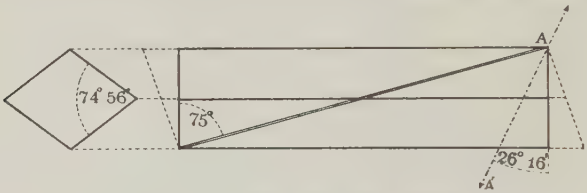


FIG. 627.—Square-ended Nicol Prism.

inclined 74° instead of 68° to the natural long edges, and the latter have then also been trimmed to follow to the same extent. The effect is to throw back the blue band and to widen the field.

In order to avoid loss of light by reflection from the oblique end-faces small Nicols are often made "square-ended," that is, with the ends perpendicular to the long edges. The lateral displacement is also lessened. The angle between the optic axis and the end-face is then 26° 16′, and the section-plane is usually made 75° to the end-face. Each end is a rhombus showing the rhombohedral angle of calcite, 74° 56′. Such a prism is represented in Fig. 627.

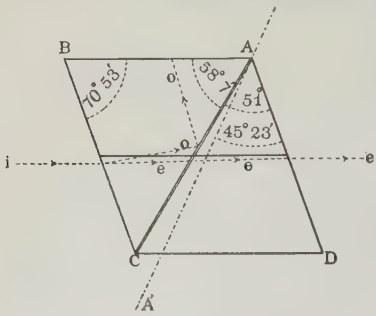


FIG. 628.—Foucault's Prism.

Foucault's Prism.—In this calcite polarising prism a film of air replaces the balsam joint, and one-third the spar suffices. The faces are the natural ones of the cleavage rhomb, as shown in Fig. 628, and the section makes an angle of 58° 7′ with the basal edge AB and 51° with the end-faces AD or BC. The incident ray *i* is as usual broken up into an ordinary and an extraordinary ray on entering the crystal; the more refracted ordinary ray *o* meets the air layer at an angle greater than the critical angle, and so is totally reflected, while the extraordinary ray *e* is transmitted. The maximum internal angle of separation of the two limits, however, is only 5° 14′, corresponding to an external field of 8°. There is also a loss of ten per cent. of light by reflection at the two uncemented surfaces. The limitation of a convergent beam to

only 8° for complete removal of one of the rays is the chief drawback of the prism, which is otherwise very economical of spar. Square-ended Foucault prisms are often made, known as Hofmann's or Soret's prisms, which are useful when very convergent light is not required. Their angular field varies from 7° to 8°.

Prazmowski-Hartnack Prism.—This jointly devised prism is a rectangular parallelepipedon of Iceland spar, and the section is made from edge to edge instead of diagonally, affording a larger area at which the transmission of the extraordinary ray can occur. In order to throw back the blue band as far as possible the section plane is made perpendicular to the optic axis. As will be obvious from the plan and elevation given in Fig. 629, which also show the shape of the original rhomb from which the prism is cut, the construction is exceedingly wasteful of spar, and the cost is three times that of a Nicol. It has the advantage, however, of transmitting a much wider angular beam, its width of external field attaining a maximum of 41° 54′ when linseed

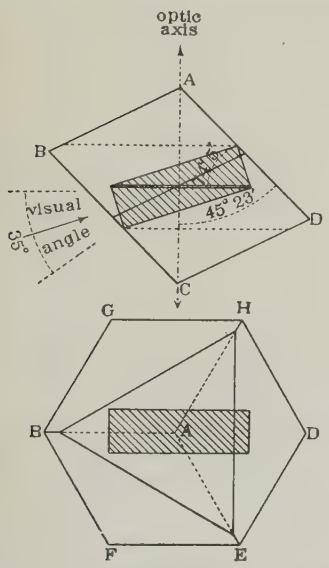


FIG. 629.—Prazmowski-Hartnack Prism.

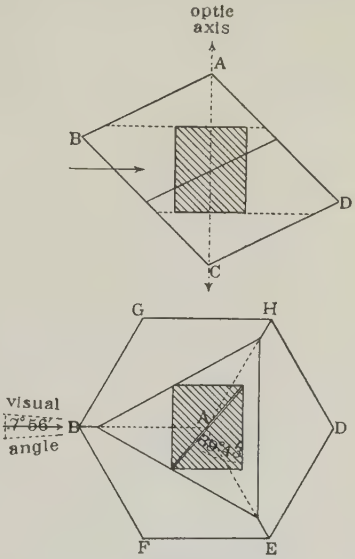


FIG. 630.—Glan-Foucault Prism.

oil is employed instead of a film of Canada balsam, the angle between the end-faces and the section being then 76° 5′. The prisms of this type usually supplied by the instrument makers have an obliquity of section to end-face of 74° 5′, and afford an angular width of external field of 35° 0′.

Glan-Foucault Prism.—This is a square-ended Foucault prism (with air film) so orientated that the section-plane is a principal section, that is, contains the optic axis. The accompanying plan and elevation given in Fig. 630, showing both the prism and the original crystal, will render the orientation clear. The angle between the end-faces and the section is 39° 43′. These prisms are light and small for their aperture, but the useful field width is only 7° 56′, and multiple reflection is apt to occur, as with all air-film prisms, at the section-surfaces.

Thompson Prism.—In this prism devised by S. P. Thompson [1] the section-plane is

[1] An excellent account of the late Prof. S. P. Thompson's contributions to our knowledge of polarising prisms will be found in the report of a lecture delivered by him to the Optical Convention of 1905.

parallel to a principal section, and the optic axis lying in it is at right angles to the direction of vision. The more recent form of it also has square ends, and is shown in Fig. 631. When Canada balsam is used as cement the angle of field is about 33°, but if linseed oil be used it is increased to 41° 50′. The square-ended form is particularly satisfactory as regards producing a field in which the planeness of the polarisation is as perfect as has yet been obtained. The angle between the film and the end-face is 76° 5′.

Ahrens Prism.—In the year 1886 Ahrens introduced a triple prism of calcite embodying the same theoretically advantageous principles as Thompson's, but consisting of three wedge-shaped pieces cut from the same rhomb. A rectangular block, the long sides of which are 1·8 times the sides of the square ends, is first cut out of a rhomb of calcite, so that the optic axis is perpendicular to one pair of the long faces, the end-faces and the other pair of long faces thus being principal sections. The block is then divided into three wedges as shown in Fig. 632, and after polishing the surfaces are cemented together into the original block with Canada balsam. The ordinary ray is reflected in this prism to both sides, and the useful internal field-angle is about 26°, the same as the internal angle of usefulness of Thompson's prism. But it has the advantage that the length for this angle is only half that of a flat-ended Nicol. This prism acts splendidly as a polariser, where alone a large prism is imperative,

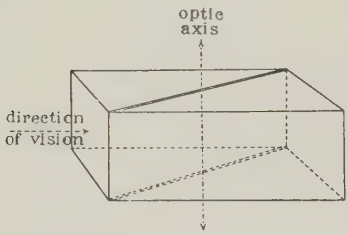


FIG. 631.—Thompson Prism.

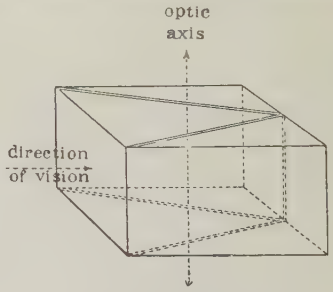


FIG. 632.—Ahrens Prism.

but not so well as an analyser, as the edge of the middle wedge is apt to produce slight distortion of the images of polarised objects. This disadvantage is more or less got rid of, however, if the end be covered with a cemented cover-glass. The external angle of usefulness of this prism amounts to nearly 60°.

Projection in Polarised Light with Nicol or other Calcite Prisms.—A large polariser is essential for projection purposes, but a very large angle of usefulness is not indispensable, as the rays from the lantern are preferably parallelised before passing through the polariser, by adjustment of the distance of the condenser of the lantern from the electric arc or other source of light, advantageously aided, in order not to have to place the condenser very near to the hot arc, by a convexo-concave lens mounted next to the entrance end of the polariser. The concave lens of the author's polarising Nicol is seen in Fig. 637, page 859, lying against the base; it is mounted in a cap which screws into the receiving end of the prism mount, that having the bevelled divided circle. The inner annulus which holds the lens in the cap may be readily unscrewed and removed, having a milled edge, in the event of the replacement of the lens by a glass plate being desirable. When convergent light is required, the convergence of the beam is always effected subsequently by a converging

system of lenses. What is essential in a polariser, however, is a prism large enough to transmit the whole of the parallelised beam, the diameter of which is about two inches, the usual size of objects for the lantern polariscope for parallel light being about $1\frac{5}{8}$ inch in diameter. A large ordinary Nicol prism is the most efficient of all polarisers in the author's opinion, but if such be not available, one of the other forms described may be employed instead. As analyser, a prism affording a wide angular field is necessary, as the rays leave the projecting lens with considerable convergence ; but it is not essential to have a large analyser, as the convergent cone forms its apex about where the prism is introduced

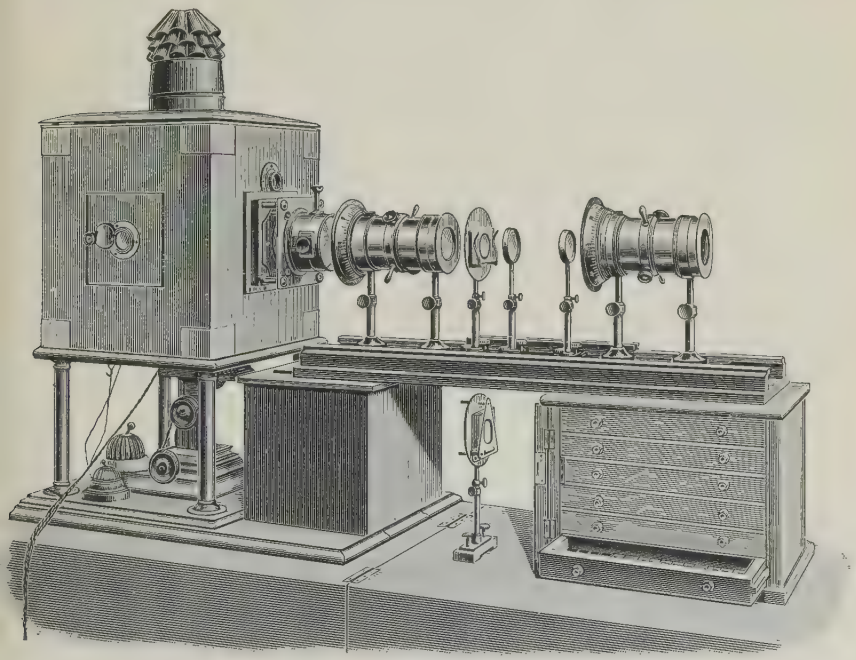


FIG. 633.—Projection Polariscope arranged for Parallel Light.

The author finds a large Nicol, however, the companion to the polariser, also the most efficient analyser, when the matter is considered from every point of view, including projections in convergent light and the projection of experiments of all kinds in polarised light. But for many purposes a much smaller prism of wide angle, such as almost any of the forms with flat ends described in the preceding pages, will serve equally well. If, however, the large Nicol analyser be available, there is no object in replacing it by any of these, and none can surpass it for brilliancy of field.

The author's projection polariscope, as arranged for projections of ordinary objects in parallel light, is shown in Fig. 633.

The lantern, water-cell, and optical bench are as already described and shown in Fig. 615, page 838, but both the large Nicols are now employed, the polariser having

its convexo-concave parallelising lens at the end nearest to the water-cell, with its convex side nearest to the latter. After the polariser comes the rotating object stage, with aperture of $1\frac{7}{8}$ inch diameter, and spring-clips to take the mahogany frames of the standard size ($2\frac{1}{4}$ by 4 inches with clear aperture of $1\frac{5}{8}$ inch diameter and rabbet of 2 inches diameter), in which the quartzes, selenites, micas, and crystal objects for the projection polariscope are usually mounted. The objects are cemented with balsam on a glass plate, or between a pair of glass plates, of $1\frac{7}{8}$ inch diameter, which just fit in the rabbet, and are secured by a spring-annulus of brass wire. An alternative stage, not rotating, but having a spring front of such latitude of spring as enables as many as three objects to be held at once, is shown in the recess under the optical bench. It is very useful when besides a polarising crystal it is desired to use a quarter-wave mica plate in front of, and a second one behind, the crystal. After the stage come two plano-convex projecting lenses, which form a very effective practically achromatic combination, the first either of 6 inches or 5 inches focus, the latter generally preferable, and the second of $8\frac{1}{2}$ inches focus. The stage and the lenses are each separately mounted on a standard adjustable for height, rotation, and transverse motion, the latter by means of a sliding dove-tailed base moving in a similarly shaped brass guiding bed, mounted in turn on the mahogany longitudinally narrow but transversely long slider in the optical bench. Each of these sliding bases is provided with two milled-headed fixing screws. Lastly comes the analysing Nicol. For convergent light work a special set of lenses is used, described in Chapter XLIX. and shown in Fig. 779.

The apparatus may also be used as a very efficient **Table Polariscope**, in the manner illustrated in Fig. 634 as regards the arrangement for parallel light. The two large Nicols, the object stage, and a large viewing lens, are the essential parts, together with a source of white light.

The concavo-convex parallelising lens at the receiving end (left in Fig. 634) of the polarising Nicol is replaced by a finely ground glass plate, to distribute the light evenly over the field. The source may, of course, be ordinary day- or sunlight reflected simply from an inclined sheet of white cardboard, but the author finds it usually more convenient to employ an electric lamp of about 40-50 candle-power, or still better one of the 120-candle-power half-Watt lamps referred to on page 39. It is contained in the mahogany box shown at the left end of the apparatus, which is lined within with metal and terminates above in a ventilation chimney: there are also holes in the bottom of the box to facilitate the ventilation, and a window in front and a door behind. The amount of heat reaching the polarising Nicol from the lamp is thus rendered a minimum and harmless. It is the same box as is referred to in Chapter XLIV., containing within it also the arrangement there described for bringing automatically any one of three platinum boats containing salts of lithium, sodium, and thallium into a Bunsen flame, which may replace the electric glow-lamp when the spectra of coloured flames are required, as during the calibration of the monochromatic illuminator.

The viewing lens is either the one shown at the right end of the polariscope in Fig. 634, a simple lens of $4\frac{1}{2}$ inches diameter and 11 inches focus, or an achromatic combination of about the same diameter and equivalent focus; the former appears to afford as good results as the latter for most purposes, and, after using both, on the whole the author prefers the simple lens. The rotating object stage is the same as that shown in Fig. 633, but it is shown in Fig. 634 with a second fixed stage fitted immediately behind it, cut out of hard mahogany. It was made for the experiment described in Chapter L. and illustrated in Fig. 806, for the reception of the slide containing two large section plates of respectively right- and left-handed quartz each one millimeter thick; this slider is actually shown in Fig. 634 lying on the optical bench underneath the polarising Nicol, where it has been laid after using it in position in the fixed

stage, to demonstrate by sliding it to and fro the respective right- and left-handedness of the two quartzes, with the aid of the 24-sector mica which is shown in position on the rotating stage. This second stage proves so useful for many other experiments also, that the author usually leaves it in position as shown in Fig. 634, but it can readily be removed when desired, as it is merely fixed by the sliding of dove-tails, which it carries at its lower end, into correspondingly shaped morticings in the side of the transverse basal slider on which the whole object-carrying apparatus is adjustably mounted.

The Double-image Prisms of Rochon and Wollaston.—Besides the polarising prisms of calcite described in the foregoing pages, there are two other extremely useful prisms constructed of this important mineral,

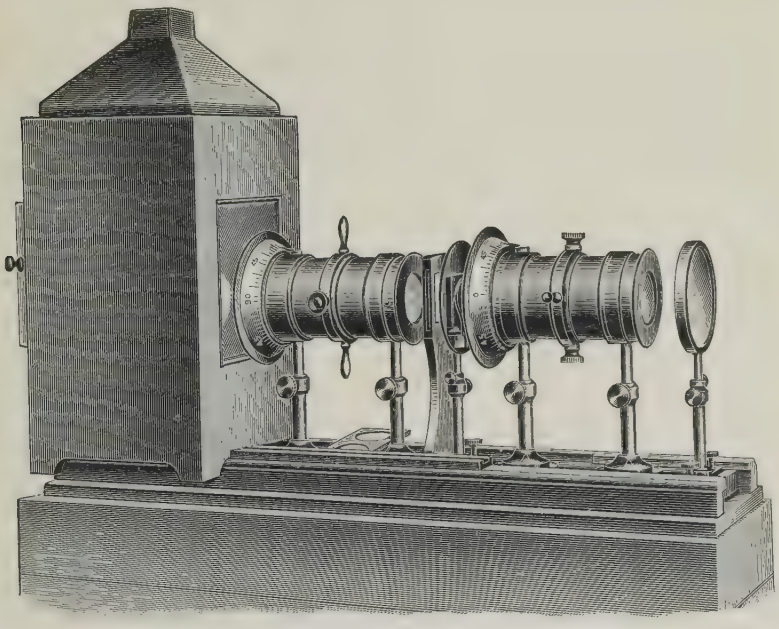
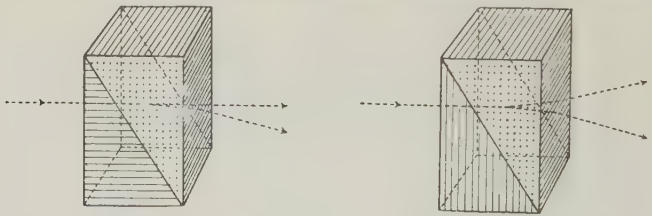


FIG. 634.—The Arrangement as Table Polariscope.

known as "double-image" prisms, their purpose being to separate the ordinary and extraordinary rays more than can be done with a simple rhomb in the manner described on the first page of the last chapter. It was there also shown that if we use a 60°-prism (two truly plane and polished faces inclined at an angle of about 60° being the essentials of such a prism) the two rays are more separated and the divergence increases as the screen is approached on which the two spectra are thrown. If we make the prism angle not so great as 60°, somewhere between 30° and 50°, according to the amount of separation desired, we can neutralise the chromatic dispersion of each image more or less by means of a similar wedge of glass, cemented to the calcite prism by balsam so as to make the whole into a rectangular block. The two images of the aperture in front of the lantern condenser then appear on the screen practically uncoloured.

Better achromatism, however, is effected if both wedges are made of calcite, and there are two methods of cutting the second achromatising prism, one of which, that due to Wollaston, gives twice as much separation of the images as the other, that of Rochon, but with less perfect freedom from colour. In both these prisms the essential wedge-prism (the right-hand one in both the figures) is cut with its refracting edge parallel to the axis of the crystal, the condition for maximum separation. These two types of double-image prisms are diagrammatically shown at *a* and *b* in Fig. 635, *a* representing the Rochon prism and *b* the Wollaston type, the shading indicating the direction of the optic axis.

Rochon's Prism.—In this prism the achromatising wedge has the optic axis perpendicular to the refracting edge, and parallel to the direction of transmission of the light, as shown by the shading at *a* in Fig. 635. The rays pass through this wedge, therefore, unaffected, the incidence being normal and the ray passing along the axis of no double refraction. The vibrations thus occur perpendicularly to the axis, and equally in all directions of the circular section around it. In the second wedge double refraction occurs, but the ordinary ray goes through undeflected, while the extraordinary ray is deviated. When the prism is rotated about the direction of the



(*a*) Rochon Prism. (*b*) Wollaston Prism.

FIG. 635.—The two Double-image Prisms.

incident ray as axis, the image on the screen due to the extraordinary ray rotates about that due to the ordinary ray, which remains fixed. A Rochon prism used in an actual experiment described on the next page is shown in Fig. 636.

Wollaston's Prism.—The only difference from Rochon's prism is that in Wollaston's the first wedge has the spar rotated a right angle so that the light is incident on the other rectangular face of the wedge, bringing the optic axis perpendicular to the direction of the incident light as well as to the refracting edge. The incident ray is thus divided into two rays immediately in this first wedge, one vibrating parallel to the axis and the other at right angles thereto, the former being an extraordinary and the latter an ordinary ray. The effect is to cause both rays to issue deviated from the second wedge, and thus to afford double the separation of the images afforded by Rochon's prism, as will be clear from *b* in Fig. 635. For, the principal planes of the two wedges being at right angles, the ordinary ray received undeviated from the first wedge traverses the second wedge with the velocity and refraction of the extra-ordinary one, its vibrations being now parallel to the axis, causing that ray (the ordinary) to be as much refracted as the extraordinary one proper, thus doubling the total refraction. The two rays are equally deviated on opposite sides of the normal, and when the prism is rotated about the direction of the normally incident light both images revolve round the centre of the line joining their own centres.

Many uses will be found for double-image prisms during the course of optical work in crystallography, but one of the most instructive and striking experiments may be referred to here, and is illustrated in Fig. 636.

Two images will obviously be thrown on the screen, when either a Rochon or a Wollaston prism is interposed in the beam of light leaving the lens, which focusses on the screen an image of a circular aperture in an opaque diaphragm placed in front of the lantern condenser. These images are composed of rectangularly plane-polarised light. That is, the planes of polarisation of the light composing them are at right angles. Hence, when a Nicol prism is placed between the lens and the double-image prism, as shown in Fig. 636, or indeed anywhere in the path of the beam of light before the deviation has become too great for both rays to get through the Nicol, one image will be found to extinguish at one position of the Nicol in its revolution, and the other at 90° from that position, while midway at the 45° positions both images will be transmitted with partial intensity. Next, when a polarising crystal, such as an evenly polarising film of gypsum (selenite), is introduced between the double-image prism and the Nicol, preferably close up to the former, the two images will be coloured complementarily, with the brilliant colours for which selenite is famous in polarised light, when the film has been rotated to the position for maximum brilliancy. That the colours are truly complementary, moreover, is absolutely proved at the same time, by the fact that when the two images are made partially to overlap —which is only a matter of choosing an aperture of the convenient size from among the four afforded by the diaphragm—the overlapping portion is quite colourless, being illuminated by brilliant white light. Thus, for instance, a so-called " blue-and-yellow selenite " is a film of such thickness as to afford for a certain position of the Nicol a brilliant blue in one disc and a bright yellow in the other, while the overlapping part is colourless. Similarly, a " red-and-green selenite " produces a red and a green image, with a white lenticular part where the two circular discs overlap. The discussion of the necessary thickness of gypsum, and of the reasons for these phenomena, will be entered into fully in Chapter XLII.

As regards the practical disposition of apparatus for this experiment, that shown in Fig. 636 is particularly convenient. The beam from the lantern condenser passes first through a thick water-cell carried on the lantern front, in order to remove the heat rays and thus protect the balsam cementing films of the Nicol and double-image prisms from their softening action. Next comes a large rotatable disc-stage with two-inch central aperture, serving either as object stage or, as in this experiment, as signal aperture; as an aperture two inches in diameter is too large for this experiment, and it is desirable to have a ready means of varying the size of the opening, a rotating diaphragm pierced with four apertures of $1\frac{5}{8}$ inch, 1 inch, $\frac{1}{2}$ inch and $\frac{1}{4}$ inch diameter respectively, is attached to it in front, with the chosen aperture, generally one of the smaller ones for ordinary screen distances (the half-inch being especially suitable), concentrically in front of the fixed large aperture of two inches. This diaphragm is readily removable when not required, being merely attached by a milled-headed pivot, secured behind the stage by a clamping nut and flanged in front of the stage so as to permit of ready rotation of the diaphragm and its fixation at the suitable position. Next comes the projecting lens, then the large Nicol, and lastly a large Rochon prism, one of the pair shown mounted together on the central stand in Fig. 637. The diaphragm-stage, lens, Nicol, and double-image prism are each adjustable for

height, azimuth, and transverse rectangular position on their separate pedestal stands, which are themselves capable of sliding anywhere along a grooved basal guiding bed, which affords the other rectangular movement, the longitudinal one, necessary for absolutely general adjustment. The mounting of the large Nicol on its stand will be clear from Fig. 637, where it is shown on the left; the transverse adjustment of the two supporting columns is afforded by slots in the base, which are covered by the two broad circular footplates, the columns being rigidly fixed below, after adjustment, by nuts. The selenite, a thin film of gypsum mounted with balsam between two glass

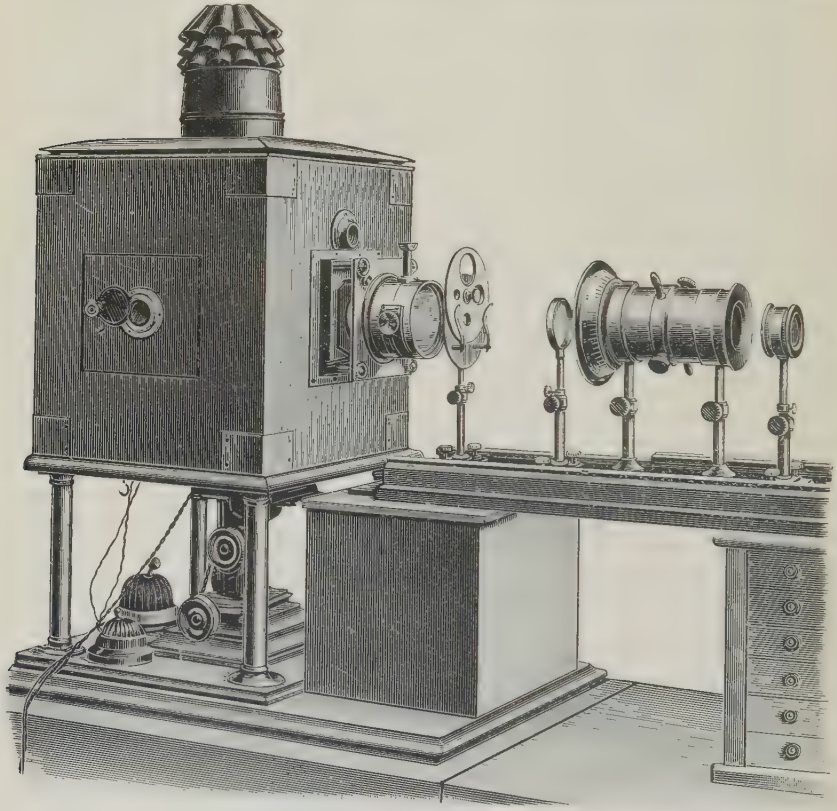


FIG. 636.—Experiment with Double-image Prism, Nicol, and Selenite Film, proving that Complementary Colours make White Light on Blending.

plates, is held in a rotating mount with outer milled flange, resembling that of the double-image prism itself except that the tube is much shorter; it fits, like that of the prism, in the same outer tube carried rigidly by the standard, both double-image prism and selenite being thus separately rotatable in this short outer tube. They can also be interchanged as regards their position, if desired, but for this experiment the selenite is fitted in the outer tube at the end nearer to the Nicol; the longer inner tube mount of the Rochon prism has a similar flange for convenience in rotating the prism.

If desired, the Rochon prism may be replaced by a Wollaston prism in this experiment, when double the amount of separation of the two images on the screen is afforded under similar conditions, and the same size of aperture may therefore be used for

a shorter working distance from the screen. Such a Wollaston prism, mounted as just described on an adjustable standard, is shown to the right in Fig. 637. The transversely adjustable base of this standard as shown in the figure (lined underneath with felt to ensure smooth sliding in the lathe-bed), and the standard itself, are typical of a dozen similar ones carrying the lenses and other accessories of the author's crystallographic projection apparatus. The selenite is carried in a slide pierced by three circular apertures, sliding in a pair of slots in a separately rotatable mount at one end of the outer tube, a spring regulating the tightness of the sliding; the Wollaston prism is rotated by means of a milled flange at the other end. One aperture of the slide is filled with a red-and-green selenite, another with a blue-and-yellow selenite, and the third is vacant, for use when it is not desired to interpose a crystal film.

Huyghens' Experiment with two Double-image Prisms. - A further

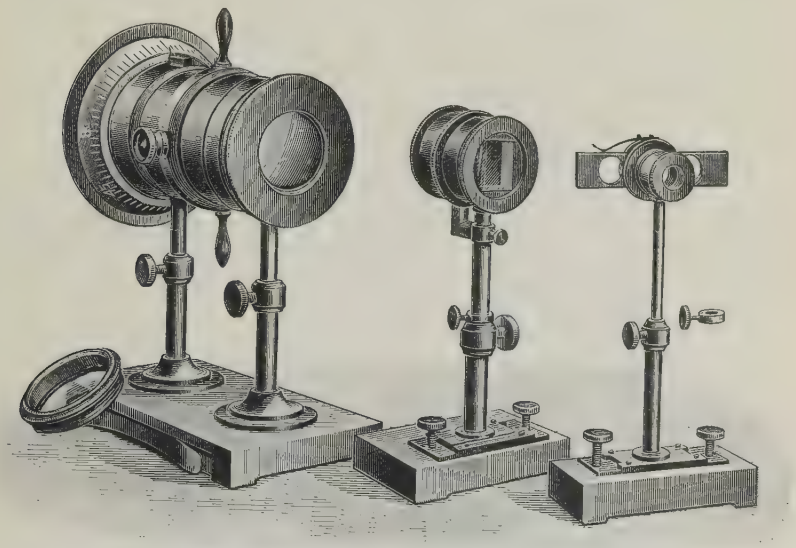


FIG. 637.—Nicol Prism with Concave Parallelising Lens (left), Pair of Rochon Prisms mounted for Huyghens' Experiment (centre), and Wollaston Prism with two Selenites (right).

most instructive experiment, requiring a pair of similar double-image prisms affording equal separation of the images, preferably of the Rochon type, is that first performed by Huyghens with a pair of simple rhombs of calcite. It is convenient that the two Rochon prisms should be so mounted that either can rotate separately or be removed altogether, and that a film of gypsum may be introduced between them and also independently rotated. Two such equal Rochon calcite prisms of $1\frac{1}{2}$ inch clear aperture, constructed for the author by Mr. Ahrens, are shown on the central stand in Fig. 637. One of these prisms and the selenite attachment have already been just described, and the second Rochon prism is similarly mounted in a flanged inner tube, rotating by means of the milled flange within an outer tube carried by an adjustable elbow-bracket sliding freely about the standard, and capable of fixation at the exact

height which brings the two prisms into line, by means of a fixing screw. This second prism is attached on the selenite side, so that the latter comes between the two Rochon prisms, not quite touching the outer tube of the second one.

A very convenient mode of performing the experiment—which requires no Nicol prism or other accessory than the projecting lens, an aperture-diaphragm, and the

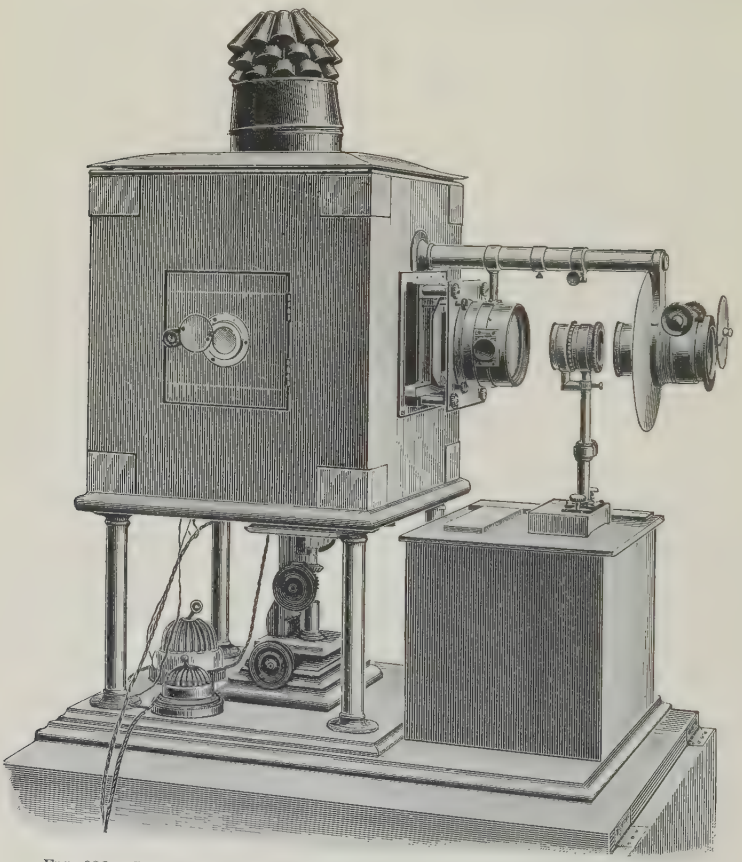


FIG. 638.—Huyghens' Experiment as performed with a Pair of Rochon Prisms.

water-cell to protect the balsam of the prisms from the heat rays by filtering them off—is shown in Fig. 638, provided the optical front of the lantern is one arranged to permit of the performance of lantern experiments, being unencumbered with any restrictive tubular support for the projecting lens. The form of lantern front adopted by the author, after experimenting with many varieties, is shown in the figure. To the front of the brass plate of the usual lantern-slide carrier-frame there is screwed a very short tube $4\frac{1}{2}$ inches in diameter for the reception of the water-cell, which may, however, be supported independently if desired, as shown later in Fig. 779, and the short tube altogether removed. From the top of this short tube there rises a little upright, termi-

nating above in a stirrup-rest for a rigid tube screwing into a socket on the lantern front above the slide frame; the outer end of this tube carries a tightening collar, to fix in any convenient position an inner tube which slides within it. This adjustable inner tube carries at its outer termination the rectangularly depending arm which supports the projecting objective. The latter consists of an achromatic doublet, composed of two pairs of lenses, of $2\frac{1}{4}$ inches aperture, the two combinations together forming an 8- or a 10-inch objective (it is convenient to possess a pair of objectives of these two focal lengths, to suit different screen distances); one combination is mounted at each end of the objective tube, which slides within an outer tube carrying a rack, this outer tube in turn sliding, for focussing purposes, with the aid of a driving pinion (provided with two large milled heads for convenience of focussing from either side) in the outermost shorter tube carried by the bracket-arm. A large convex metallic screen is also carried concentrically by the outermost tube, in order to shield off any stray light rays. The two double-image prisms on their stand are brought into the clear space between the water-cell and the objective, where there is ample room for proper adjustment. For aperture it is convenient to use the ordinary lantern-slide carrier, with a thick blackened card or brass plate $3\frac{1}{4}$ inches square, pierced by a cleanly-cut circular central aperture of about half an inch diameter. It is well to have two or three such cards or plates with apertures of larger and smaller diameters, in order that the most convenient size of image may be obtained on the screen.

In performing the experiment, the single direct image of the aperture is first focussed by the objective in the absence of the prism; the latter is then placed in position, but with the second double-image prism removed, by sliding down the arm carrying it, and the selenite is also removed from the outer tube of the other, thus leaving the first prism alone in operation. On actuating the lantern two images of the circular aperture are thrown on the screen, and when the prism is rotated the image due to the extraordinary ray will be observed to rotate around that due to the ordinary one. On adding the second prism and rotating it until it is similarly orientated to the first, the two images are observed to be still separated in the same direction—vertical when both prisms are arranged with the optic axis vertical, as indicated by a mark provided on the mount of each—but at double the distance, the two Rochon prisms being of similar angle and equal in every respect. On the least rotation of either prism from this position two other images make their appearance, making four altogether, the two new ones at first very weak, and appearing to start identically from the centre between the other two, and separating more and more so as to form with the others the corners of a rhombus of ever-widening angle, until when the prism has been rotated for 45° all four images are of equal intensity and the angle of the rhombus is also 45°. Rotating further, the first two images begin to disappear, until at 90° they have vanished and there are only two images again of equal intensity, but they are the second pair and arranged along a 45° diagonal. Rotating further towards 135° there are again four images, at 135° arranged as another rhombus of 45° angle; while at 180° there is but a single image, of double the intensity of any brightest pair. In the next half revolution similar phenomena occur in the reverse order. The whole of this interesting behaviour is entirely explained on the assumption that each prism transmits two differently refracted rays, an ordinary and an extraordinary, of which the vibrations occur in two different planes (parallel to the longer and shorter diagonals of the rhomb respectively) at right angles to each other and to the direction of transmission.

When the selenite film is also in position, there are always four images except at 0° and 180°, when all four are in the same vertical line and two of them coincide at the centre. But, except at the 45° positions, when no colour is shown and the appearance is the same as in the absence of the selenite, the images are now coloured, two red or blue and the other two the complementary green or yellow. The use of the selenite is thus to render visible the images, coloured, which are extinguished in the absence of

a crystal film. The whole phenomena will be rendered clear by the diagrams given in Fig. 639.

The actual effect drawn is that which was observed when a black circular blot on a sheet of otherwise clean white blotting-paper was viewed directly through the Huyghens apparatus. A white spot on a black ground answers equally well. The arrows indicate the direction of the optic axis, and the dotted rhombohedral outline indicates the original rhomb from which each prism was cut. The upper row of five figures represents the phenomena without selenite, and the lower row what occurs when a red-green selenite is introduced, the colours being the complementary, when the white spot on a black ground is used, to those observed when the spot is black on a white ground. The first (top left) figure represents the two images of the spot seen when the prisms are parallel, o being the immovable ordinary image and e_2 the extraordinary. The intermediate dotted ring e_1 indicates the position of the extraordinary image when only one prism is used, the separation then being only half as much. When the selenite is introduced all three images appear, o and e_2 green and e_1 red, as shown in the left lower figure. The second upper figure exhibits the appearance when the front prism has been rotated 45°. There are four images of equal intensity, but only half as

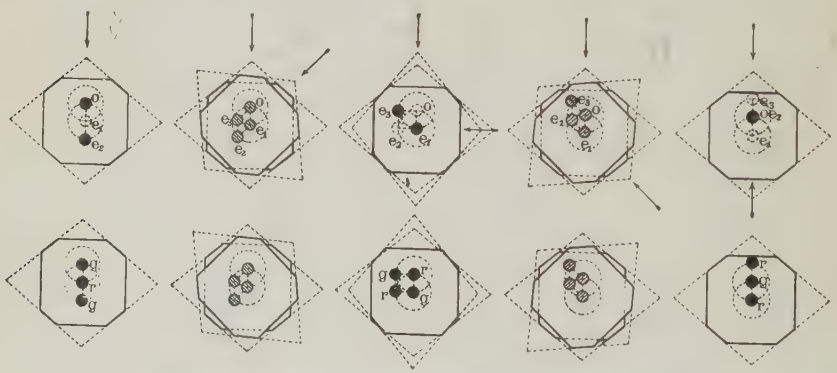


FIG. 639.—Images of a Black Spot afforded by a Pair of Double-image Prisms, one of which is rotated.

strong as the two in the first figure ; e_2 has become deflected to correspond to the 45° rotation, e_1 has become visible, and a third extraordinary image e_3 has been formed by resolution out of o, which is thereby diminished in intensity. No change occurs for this position on adding the selenite, no colour being developed. The third upper figure indicates the extinction of o and e_2, and the brilliant full intensity of e_1 and e_3, when the front prism has been rotated 90°. When the selenite is added (third lower figure) all four images appear at the corners of a square, o and e_2 red and e_1 and e_3 green. The fourth figures indicate the four half illuminated images for the 135° position of the front prism, and the two last those for the 180° position. Without the selenite there is now only a single image, o and e_2 overlapping, for the front prism now reverses the deflection of the image e_2 by the first prism, and o remains immovable at the centre ; e_1 and e_3 are extinguished, but they appear, coloured red, when the selenite is introduced, the overlapping o and e_2 images being both green.

The phenomena may be interpreted very simply as follows.

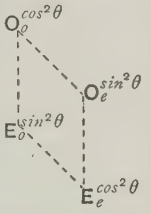
Two of the four images of the circular aperture or spot occupy the same positions as if only the first prism or thick plate were acting, while the two other images are displaced from these positions along the

direction of the principal section of the second prism or plate. If we accept the assumption that the ordinary ray is polarised parallel to the principal section (the vibrations being therefore perpendicular to the principal section), and that the extraordinary ray is polarised perpendicularly to the principal section (its vibrations occurring in that section), and if we call the ordinary and extraordinary images afforded by the first prism or plate alone O and E, then O becomes O_o and O_e after passing also through the second prism or thick plate, and E becomes E_e and E_o.

Now the amplitudes of the rays composing the images O_o and O_e stand to each other in the same relationship as the cosine and sine of the angle of rotation θ of one prism or plate with respect to the other, that is, to the angle between the principal sections of the two prisms or plates. Consequently, as the intensity varies as the square of the amplitude of the vibration, the intensities of illumination of the two images vary as $\cos^2 \theta$ and $\sin^2 \theta$. Similarly, the intensities of E_e and E_o also vary as the squares of the cosine and sine of the angle of rotation of one prism or plate with respect to the other. The intensities of O and E are themselves each the half of the intensity of the incident light, neglecting the small loss by reflection and absorption, the latter being almost *nil* in the case of calcite.

Now in the special cases when $\theta = 0°$ or 180°, that is, when the prisms or plates are parallel, only E_e and O_o remain visible; for as $\cos^2$ (0° or 180°) = 1 and $\sin^2$ (0° or 180°) = 0, the intensities of the images (O_o and E_e) depending on the square of the cosine have their full unit intensity, while those (O_e and E_o) depending on the square of the sine have no intensity at all, that is, are extinguished. Thus O becomes only ordinarily refracted in the second prism and E only extraordinarily refracted. At 180° the two persisting images O_o and E_e overlap, when the prisms or plates are equally thick, as the extraordinary ray suffers two opposite displacements in the two plates.

When $\theta = 90°$ or 270°, the two principal sections being then perpendicular to each other, only O_e and E_o remain visible, O_o and E_e being extinguished. O in this case becomes only extraordinarily refracted and E only ordinarily refracted in passing through the second prism or plate.



At the 45° diagonal positions of the second plate with respect to the first, as cos 45° and sin 45° are each equal to $1/\sqrt{2}$, the intensities of all four images are equal. The positions of the four images at the corners of a 45° rhombus, and their values, may then be graphically expressed by the simple scheme shown in the margin.

Bertrand's Calcite Prism.—This remarkable prism, also termed Bertrand's Idiocyclophanous Prism, is very simply prepared out of a single rhomb of calcite, and has the interesting property of exhibiting the uniaxial interference figure directly to the naked eye, when held before and fairly close to the eye, between it and a bright light such as that of the sky, and looking through the prism towards the latter. Indeed, two such

figures are seen side by side, the one being that usually shown by a plate perpendicular to the optic axis in convergent polarised light when the Nicols are crossed, namely, a black cross and circular iris-coloured rings; while the other is the figure afforded when the Nicols are parallel, that is, a white cross and the iris rings No Nicols are required with Bertrand's prism, which itself affords the phenomena directly. On moving the prism slightly from side to side in front of the eye, either figure can be brought apparently central in the field, and to occupy the other's place. When both are in view at once they are usually somewhat more distant in the horizontal line from each other than the diameter of either figure.

The essential conditions on which the construction of the prism depends are the three following: (1) There must be two internal reflections, between which the light must traverse the direction of the optic axis; (2) the two reflecting plane surfaces must be parallel to each other, and inclined at about 45° to the optic axis; (3) the light should enter and leave the calcite by two other plane and parallel surfaces which are principal section-planes, (containing the optic axis). The plan of the prism is thus a parallelogram of somewhere about 45° and 135° angles. Condition 2 is adequately fulfilled by cleavage surfaces, for the angle between the optic axis and the normal to the cleavage face (the cleavage being parallel to the primary rhombohedron $r\{100\}$) of calcite is 44° 37′ (it is the angle r : (111) on page 378). The other two essential surfaces referred to in condition 3 are prepared by cutting, grinding, and polishing.

The simplest mode of constructing the prism is to take a cleavage rhomb of somewhat tabular form, that is, having one parallel pair of the cleavage surfaces closer together than the two surfaces of each of the two other pairs, such a rhomb, in fact, as ABCDEF, of the left-hand drawing at *a* in Fig. 640. The two parts BGH and DKL, as represented at *b* in Fig. 640 with the rhomb turned round sideways, are then cut off; the cutting occurs along the planes GH and KL, each of which is parallel to the optic axis and to the other section plane. The result, the shaded remainder, is shown also separately at *c* in Fig. 640, which represents Bertrand's prism as completed. In order to render the mounting of the prism more convenient it is usual to cut away also the ridge EF and the corresponding one on the other side, parallel to the plane of the paper. The mount is usually of cork, and after insertion of the prism the cleavage reflecting surfaces HC and AK are screened off by means of blackened cardboard or thin sheet brass, so as to leave only the cut and polished surfaces GH and KL for the entrance of the light from the sky or other bright source and its exit to the eye. On holding up the prism to the light, so that the surface KL is nearest to the eye (one to two inches distance from the latter being usually the best position), and the face GH facing and nearest to the sky or other strong light, the two uniaxial figures are at once seen, the figure with dark cross on the right and that with the white cross to the left, the two being separated at a distance which, in the Bertrand prism made by Ahrens for the author, is slightly more than the diameter of each of the figures. The path of the light will be clear from the right-hand drawing *c* of Fig. 640. Entering more or less

normally at the face GH, it is reflected at the cleavage surface AK; it then traverses the crystal along the optic axis, is again reflected from the second cleavage surface HC, and leaves the prism approximately normally to the face KL, to enter the eye.

The theory of the prism is discussed by Mascart in his *Optique*, vol. ii., page 196, but does not appear to have yet been altogether satisfactorily understood.

A similar prism in quartz was constructed by Ahrens about the year

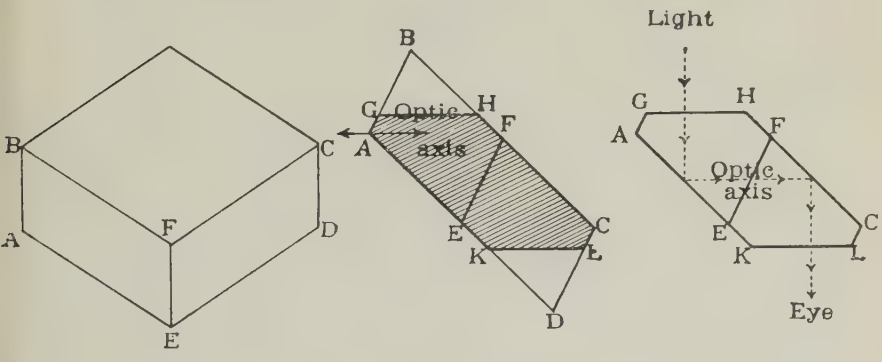


FIG. 640.—Bertrand's Calcite Prism.

1896 for Prof. Silvanus Thompson, but the effect with quartz is not so good, a much greater length of path being necessary. There are no definite crosses afforded, and the rings are very faint, being of a high order.

Dove's Calcite Prism.—This is an erecting prism of calcite which will be found described on page 813 of Chapter XXXVII.

Jellett's Compound Calcite Prism.—This is a prism employed instead of a biquartz, as a device to enhance the sensitiveness of the determination of the rotation of the plane of polarisation of light, and a description of it will be found in Chapter L. dealing with that subject.

CHAPTER XLI

THE TRANSMISSION OF LIGHT THROUGH BIAXIAL CRYSTALS

In the case of a biaxial crystal, that is, one belonging to the rhombic, monoclinic, or triclinic systems, neither of the two rays into which a beam of light is divided on entering the crystal is an "ordinary" ray, in the strict sense of the term as applied to uniaxial crystals; for neither obeys the law of sines, except when moving along one of the three rectangular axes of the optical ellipsoid. This, however, is always arranged to occur with a 60°-prism prepared, for refractive index determinations, with the aid of the cutting-and-grinding goniometer described in Chapter XLIII. For it is quite easy with this apparatus to grind the two surfaces of the prism so that the light transmitted at minimum deviation shall travel along one of the three axes of the ellipsoid, and so that the vibrations of the two rays into which it is decomposed shall occur parallel to the two other rectangular axes. Two such prisms, the refracting edges of which are parallel to two different axes, and the bisecting planes of which are parallel to two different principal planes of the ellipsoid, fulfil these conditions, and together will afford all three refractive indices, and one of them in duplicate. Thus one prism may afford α and β, and the other β and γ, in which case α and γ are furnished once and β in duplicate; or one of the prisms may afford α and γ, instead of either of the two pairs just mentioned, when either α or γ will be obtained in duplicate. Close agreement of the duplicate values will offer an excellent guarantee of the accuracy of the work.

The **wave-surface** of a biaxial crystal is a surface of the fourth degree composed of two shells, one within the other. These two shells touch each other at four points, which are at the bottom of depressions in the outer shell and on the summits of protuberances on the inner one. The depressions or pits are of such a character that a tangent plane to the surface to cover them touches the surface along a circular line of contact. Except for these depressions and protuberances where actual contact occurs the two shells resemble ellipsoids of general triaxial form. Indeed it is common to regard the shells as two separate wave-surfaces. The four points of contact are common points on the two shells where the two "**Optic Axes**" emerge, which cause the crystal to be termed "biaxial," each optic axis passing through the centre and through two

of the points of contact on opposite sides of the centre. In Figs. 641 and 642 an attempt is made to give a correct idea, at first somewhat difficult to grasp, of the real nature of the two shells of the wave-surface of a biaxial crystal. In Fig. 641 the top-left-front octant of the outer shell has been removed, revealing the inner shell and the nature of the sections by the three rectangular principal planes, the axial planes of the optical ellipsoid. The drawing was made from an excellent model by Krantz, which can be taken to pieces, the three principal section-planes just referred to having been actually cut through. The upper half of another model in plaster is shown in Fig. 642, the two quarters of the outer surface being separated sufficiently on each side of the half of the inner surface to reveal the latter clearly, its protuberances being indicated by the shading. The circular line of contact of the outer surface about the depression with a tangent

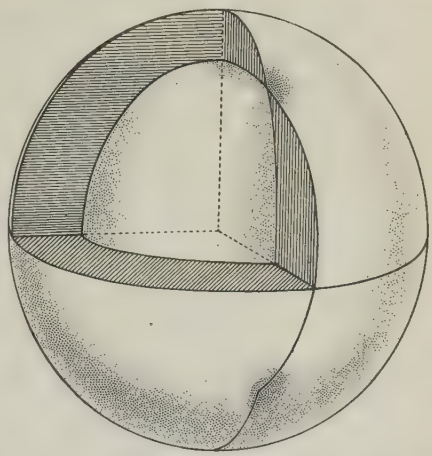


FIG. 641.—Krantz Model of Wave-surface of Biaxial Crystal.

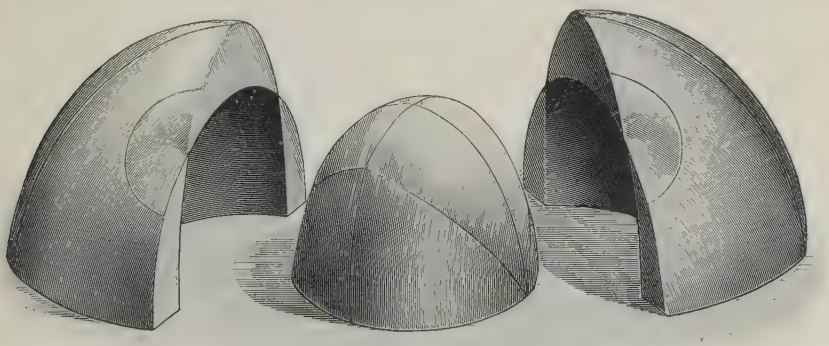


FIG. 642.—Plaster Model of Wave-surface of Biaxial Crystal, showing separated Half of Inner Shell.

plane is also shown, as well as lines indicating the positions of the chief sections. The three principal section-planes are also diagrammatically represented in Figs. 643, 644, and 645, and their relationship in one octant in Fig. 646. Lastly, in Fig. 647 all three section-planes are shown at once in a manner which will render their relationship clear.

The sections of the wave-surface by each of the three rectangular planes of the optical ellipsoid consist of an ellipse and a circle, one inside

the other in the cases of two of the sections, but one intersecting the other at the four points of contact of the shells in the case of the third section, that by the plane AOC. The lines Op joining these four points p (Figs. 644 and 646) to the centre O are the two optic axes, or, more precisely, the two "**Secondary Optic Axes.**" The distinction between

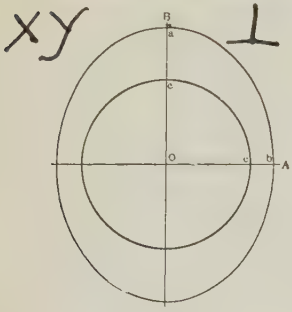


FIG. 643.

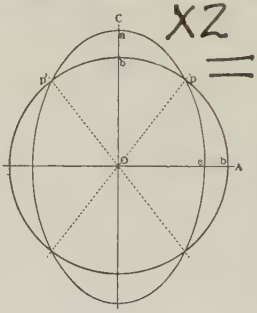


FIG. 644.

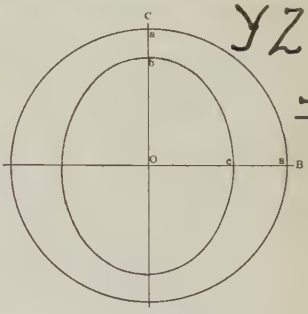


FIG. 645.

Three Principal Section-planes of Wave-surface of Biaxial Crystal.

primary and secondary optic axes will be thoroughly investigated later in the chapter, and it will be sufficient to say here that the distinction is rarely possible to be effected practically, the optic axes observed in the interference figure in convergent polarised light covering in the vast majority of cases both kinds of axes, the angle between the primary and the secondary optic axis on each side of the bisecting plane being less

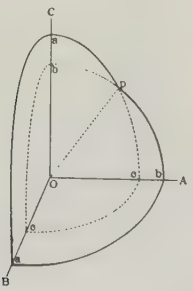


FIG. 646.—Octant of Biaxial Wave-surface showing Principal Sections.

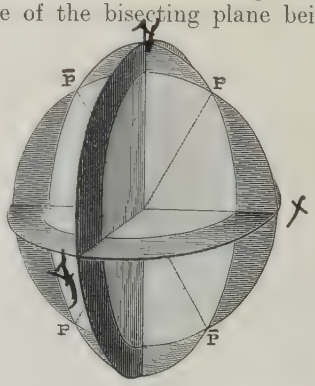


FIG. 647.—Principal Section-planes of Wave-surface of Biaxial Crystal.

than the usual error incident to the determination of the position of the optic axis. It may be useful, however, to turn here for a moment to p. 882, where the discussion occurs and a further diagram, Fig. 655, of the section-plane AOC will be found, in which both kinds of optic axes are elucidated, Omn and $O\bar{m}\bar{n}$ being the "**Primary Optic Axes**" and Op and $O\bar{p}$ the secondary, the small angle between them (grossly exaggerated in the figure) being approximately (rather more in the case drawn in Fig. 655) one half of that of the "**Cone of Inner Conical Refraction,**" mOm'.

It has been necessary in these illustrations to exaggerate the double refraction very grossly in order to render the subject at all clear. To correct the false impression thereby inevitably conveyed, the actual relative dimensions of the two wave-surfaces of a biaxial crystal with exceptionally large double refraction are given in Fig. 648, which represents a section, that containing the maximum and minimum axes of the optical ellipsoid and the optic axes, of the wave-surface of ordinary dextro tartaric acid, $C_4H_6O_6$, which crystallises in the sphenoidal class of the monoclinic system, and is an enantiomorphous substance exhibiting optical activity. Its refractive indices are $\alpha = 1{\cdot}4961$, $\beta = 1{\cdot}5359$, $\gamma = 1{\cdot}6055$, and its double refraction $\gamma - \alpha = 0{\cdot}1094$. The figure is reproduced from the data obtained by Kohlrausch in an elaborate investigation. The plane of the optic axes, the section-plane, is perpendicular to the symmetry plane {010}. A typical crystal of tartaric acid has already been illustrated in Fig. 211, page 255. The double refraction is positive, which will be shown later to mean (as already mentioned on page 832) that the α and β indices of refraction are closer together than the β and γ indices, and that the direction of vibration affording the maximum index γ is the acute bisectrix of the optic axial angle. This direction lies in the symmetry plane, in the acute angle between the crystallographic axes a and c; it is represented consequently in the figure by the same horizontal dotted line as stands for the trace of the symmetry plane, and marked γ. The vertical diameter represents the symmetry axis b normal to the symmetry plane; it is the vibration direction which affords the minimum index α. The third rectangular axis of the optical ellipsoid affording the intermediate refractive index β is normal to the plane of the paper. It is easy to see that a beam travelling along the horizontal diameter will be composed of two rays vibrating respectively parallel to the vertical diameter and normally to the paper, their velocities being inversely proportional to α and β, that is to $\frac{1}{\alpha}$ and $\frac{1}{\beta}$. The former consequently gets further from the centre of disturbance than the latter in the same time, and the respective curves are marked with these fractions. Similarly a beam travelling along the vertical diameter is resolved into two rays vibrating respectively horizontally and normally to the paper, with velocities $\frac{1}{\gamma}$ and $\frac{1}{\beta}$. The former is retarded behind the latter in consequence, as shown in the figure. Hence both beams have a component ray vibrating with velocity $\frac{1}{\beta}$, and the section of this wave-surface is a circle. The other two component rays

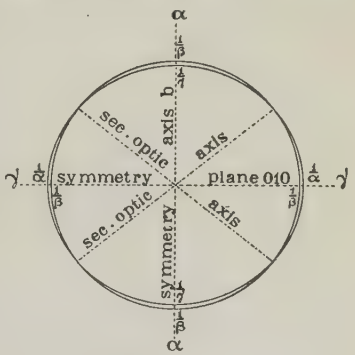


FIG. 648.—Principal Section of Wave-surface of Tartaric Acid.

correspond to the axes $\frac{1}{\alpha}$ and $\frac{1}{\gamma}$ of an ellipse, this being the form of the section of the second wave-surface. The difference in shape from a circle is very slight, but real. The broken-and-dotted lines joining the centre to the points of intersection of the circle and the ellipse are the secondary optic axes, differing by a minute angle from the primary optic axes, as indicated on page 868, both primary and secondary optic axes, however, being here as usual experimentally indistinguishable, coinciding in the optic axes as indicated by the interference figure in convergent polarised light. It will be shown later, however, in this chapter that by special devices the distinction can be experimentally verified and observed.

We saw in Chapter XXXIX. that in a uniaxial crystal there is one direction, the unique "optic axis," of either maximum (in the negative kind such as calcite) or minimum (in the positive kind such as quartz) velocity of vibration, corresponding to the conversely minimum or maximum refractive index respectively; and that perpendicular to this unique axis there are, lying in the equatorial circular section of the optical ellipsoid, an infinite number of directions of the opposite extreme of vibration-velocity or refractive index.

In a biaxial crystal, on the contrary, we have just seen that the two optic axes do not correspond to either the maximum or the minimum axial directions of the ellipsoid of optical vibration-velocity or of refractive index, but to a pair of intermediate directions, approximately joining the points of contact of the two shells of the wave-surface to the centre as above stated (these directions being the secondary optic axes), and lying in the principal elliptic section of the optical ellipsoid (as distinct from the wave-surface) the major and minor axes of which are the maximum and minimum axes of that ellipsoid and the directions of extreme refractive indices; the two "optic" axes (more precisely, the primary optic axes) are, in fact, the perpendiculars to the diameters marking the two positions where the radius vector of the principal ellipse is equal to the intermediate axis, the normal to the plane of that ellipse, as will be more clearly elucidated later in this chapter.

It is necessary to be quite clear as to the nature of the various ellipsoids that have been referred to. They are (1) the wave-surface, a true ellipsoid in the case of the extraordinary ray of a uniaxial crystal, but modified by the depressions and protuberances in a biaxial crystal, (2) the vibration-velocity ellipsoid (that of Fresnel), and (3) the indicatrix (of Fletcher). In practical crystallography we do not need to concern ourselves more with the first, the wave-surface, than is adequate to ensure our understanding its nature. It is the "velocity-of-propagation ellipsoid," representing by its axes and its *radii vectores* the propagation-velocity. There are in general two wave-surface ellipsoids, corresponding to the two rays moving with different velocities into which a beam of light is decomposed on entering a doubly refracting crystal. In the case of a uniaxial crystal they are a sphere and an ellipsoid of revolution, but in the case of a biaxial crystal the two shells together form the surface of the fourth degree already referred to. The second and third ellipsoids,

however, are alternative optical ellipsoids, the one the polar reciprocal of the other, which afford us at once a graphical expression of the experimental optical measurements, and are, therefore, of great practical importance. The third, the Fletcher indicatrix, is the most easy to grasp, as it is the direct graphical expression of the value of the refractive index for the same wave-length in the different directions within the crystal. It is now becoming more and more universally employed. The second, the Fresnel vibration-velocity ellipsoid, being the polar reciprocal of the indicatrix, is graphically expressed by plotting the reciprocals of the refractive indices. It represents what, before the advent of the electromagnetic theory of light, was formerly known as the " optical elasticity " or facility of light-vibration in the crystal, perpendicular to the direction of propagation. A ray going along one axis has the velocities of its two component rays represented by the two axes perpendicular to it, for these axes are laid down proportionally to the reciprocals of the refractive indices.

The two Varieties of the Optical Ellipsoid, the Fresnel Vibration-Velocity Ellipsoid and the Indicatrix.—Fresnel was the first to show in the year 1827 that the velocity with which the vibrations of light occur, on the passage of a ray of light through a crystal, could be expressed in general by an ellipsoid, which became, therefore, variously known as the " Fresnel ellipsoid," the " optical elasticity ellipsoid," and the " optical vibration-velocity ellipsoid." But the idea of optical elasticity became obsolete with the acceptance of the electromagnetic theory of light. The Fresnel ellipsoid will, therefore, be referred to as the vibration-velocity ellipsoid. The relative dimensions of its three rectangular axes are inversely proportional to the refractive indices along (corresponding to vibrations parallel to) those three axial directions, so that the maximum axis, distinguished by the Old English letter $\mathfrak{a}$, of the ellipsoid corresponds in direction to that for the minimum refractive index α, and the minimum axis $\mathfrak{c}$ to that for the maximum index γ, the intermediate axis $\mathfrak{b}$ corresponding to the direction to which the intermediate refractive index β applies. Also the actual values of these three axes of the Fresnel optical ellipsoid are the reciprocals of the refractive indices, that is: $\mathfrak{a}=\frac{1}{\alpha}$, $\mathfrak{b}=\frac{1}{\beta}$, $\mathfrak{c}=\frac{1}{\gamma}$. Hence, if we have determined the three refractive indices α, β, and γ, for the three rectangular directions in the crystal which are parallel to the axes of the ellipsoid, and if we express their reciprocals in the manner which has become conventional, so that the intermediate axis = 1, by dividing throughout by $\mathfrak{b}$, we have a relative measure of the three axial dimensions of the Fresnel optical ellipsoid in the ratios:

$$(1)\quad \mathfrak{a}:\mathfrak{b}:\mathfrak{c},\ \text{or}\ \frac{\mathfrak{a}}{\mathfrak{b}}:\frac{\mathfrak{b}}{\mathfrak{b}}:\frac{\mathfrak{c}}{\mathfrak{b}}=\mathfrak{a}':1:\mathfrak{c}',$$

where

$$\mathfrak{a}'=\frac{\mathfrak{a}}{\mathfrak{b}}=\frac{\frac{1}{\alpha}}{\frac{1}{\beta}}=\frac{\beta}{\alpha},\ \text{and}\ \mathfrak{c}'=\frac{\mathfrak{c}}{\mathfrak{b}}=\frac{\frac{1}{\gamma}}{\frac{1}{\beta}}=\frac{\beta}{\gamma}.$$

Now an ellipsoid which has axes the dimensions of which are relatively

expressed by the refractive indices α, β, γ themselves has been shown by Fletcher [1] to possess certain properties which render it more convenient for use as an expression of the optical properties of crystals than the Fresnel ellipsoid, and has been termed by Fletcher the "optical indicatrix." It is identical with the "indexellipsoid" of MacCullagh. The axes of this ellipsoid may either be directly expressed by the refractive indices themselves, or, in accordance with a similar convention to that referred to in the case of the Fresnel ellipsoid, designed in the cause of simplicity, the intermediate axis β may be taken as unity and α and γ expressed proportionally as follows, by dividing out by β :

$$(2)\ \alpha : \beta : \gamma, \text{ or } \frac{\alpha}{\beta} : \frac{\beta}{\beta} : \frac{\gamma}{\beta} = \alpha' : 1 : \gamma',$$

where the axial value $\alpha' = \frac{\text{index } \alpha}{\text{index } \beta}$, and the axial value $\gamma' = \frac{\text{index } \gamma}{\text{index } \beta}$.

It is customary to drop the " dashes " in these abbreviated expressions, and to state the axial ratios of the two optical ellipsoids as $\mathfrak{a} : 1 : \mathfrak{c}$ and $\alpha : 1 : \gamma$ respectively. By the "axial ratios of the optical ellipsoid," the experimental determination of which is an essential part of the optical investigation of a crystal, and which appear as important optical constants in the tabular presentation of the results of the investigation, we may thus mean either those of the Fresnel ellipsoid of optical vibration-velocity, as given in the final form of the expression (1), or those of the indicatrix, as given in the final form of the expression (2). The latter are rapidly supplanting the former in crystallographic literature, but it is perhaps advisable for the present to express the experimental results in terms of both ellipsoids, or if not, to state clearly to which ellipsoid the constants given refer. The same actual experimental work suffices for both, namely, the determination of the refractive indices for the three rectangular directions of the axes, for these directions are obviously identical for both ellipsoids. In the case of a crystal belonging to the rhombic system, as shown on page 829, these directions are also those of the three crystallographic axes. The direction of vibration of the rays affording each refractive index is ascertained by means of a Nicol prism, placed in front of the eyepiece of the spectrometer, when observing the two refracted images of the signal-slit afforded at minimum deviation by a 60°-prism, the vibration directions of which are parallel to two of the principal axes of the ellipsoid (as already explained on page 866), just as was described on page 842 with reference to the determination of the refractive indices of uniaxial crystals. Full details will be given in Chapter XLVI. of the mode of carrying out the determinations.

An example may be useful to render the mode of calculation of both sets of ratios quite clear. The case of monoclinic ammonium zinc sulphate, $(NH_4)_2Zn(SO_4)_2 . 6H_2O$, will serve, the three refractive indices of which for sodium light are: $\alpha = 1{\cdot}4888$, $\beta = 1{\cdot}4930$, $\gamma = 1{\cdot}4994$.

The axial ratios of the Fresnel optical-velocity ellipsoid are :

[1] *Mineralogical Magazine*, 1891, *9*, 278.

$$\frac{\mathfrak{a}}{\mathfrak{b}}=\frac{\beta}{\alpha}=\frac{1{\cdot}4930}{1{\cdot}4888}=1{\cdot}0028\,;\quad \frac{\mathfrak{c}}{\mathfrak{b}}=\frac{\beta}{\gamma}=\frac{1{\cdot}4930}{1{\cdot}4994}=0{\cdot}9957.$$

That is :—$\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0028 : 1 : 0{\cdot}9957$.

The axial ratios of the optical indicatrix are :

$$\frac{\alpha}{\beta}=\frac{1{\cdot}4888}{1{\cdot}4930}=0{\cdot}9972\,;\quad \frac{\gamma}{\beta}=\frac{1{\cdot}4994}{1{\cdot}4930}=1{\cdot}0043.$$

That is :—$\alpha : \beta : \gamma = 0{\cdot}9972 : 1 : 1{\cdot}0043$.

It will be observed that 1·0028 is just as much above unity as 0·9972 is below it, and that 0·9957 is as much below as 1·0043 is above unity. This reciprocal relationship between the axial values of the two ellipsoids always holds, and affords a check on the accuracy of the calculations.

The Fresnel Ellipsoid.—The velocity of light varies in a crystal not only with the direction of propagation but with the direction of vibration perpendicular thereto. Thus, let Fig. 649 represent the Fresnel ellipsoid, and O its centre, from which latter an infinite number of radii representing the vibration velocities may be supposed to proceed to the surface of the ellipsoid, their termini, in fact, tracing out the ellipsoidal surface ; also let OA, OB, OC be the three rectangular semi-axes, three special cases of such radii, arranged in descending order of vibration velocity. Then the length of the maximum axis OA or $\mathfrak{a}$ does not represent the velocity of light **transmission** along the direction OA, but the velocity of the rays which pass through the crystal with the greatest possible velocity and the **vibrations** of which occur along OA, that is, the velocity of the infinite number of rays propagated and travelling in the plane BOC at right angles to OA. It thus represents all rays polarised in the plane BOC, the direction of vibration being accepted as perpendicular to the plane of polarisation. Similarly, the minimum axis OC or $\mathfrak{c}$ represents by its length the minimum velocity, that of rays vibrating along OC but transmitted in any direction perpendicular thereto, that is, along any radius in the plane AOB. Likewise, the axis OB or $\mathfrak{b}$ of intermediate length represents the velocity of light rays transmitted perpendicularly to OB but vibrating along OB, that is, the velocity of rays transmitted along any radius lying in the principal section-plane AOC, and polarised in that plane. Hence, **the Fresnel ellipsoid represents by its radii from the centre the velocities of rays vibrating along those radii, the direction of transmission being perpendicular thereto.** It is therefore referred to as the **vibration-velocity ellipsoid.**

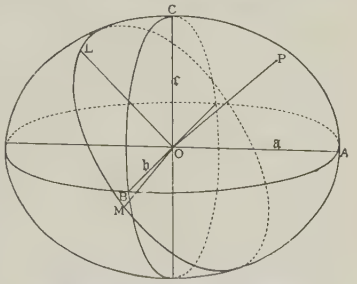


FIG. 649.—The Fresnel Vibration-velocity Ellipsoid.

Along any one of these principal axes OA, OB, OC it is possible for two rays to travel simultaneously, polarised perpendicularly to each other in the two principal section-planes which intersect in the principal

axis along which the rays are travelling, and the velocities and directions of vibration of which are represented by the two other principal axes perpendicular to the one along which the rays are passing. Thus, for instance, along OA two rays can be transmitted, polarised respectively in the planes AOB and AOC, and vibrating respectively along OC and OB.

Now as the refractive index μ for rays of light vibrating parallel to one of the three rectangular principal axes OA, OB, OC, is the ratio of its velocity in air V_a to its velocity in the crystal V_c, that is, $\mu = \frac{V_a}{V_c}$, the refractive index for each of the rays in question on entering the crystal from the air is inversely proportional to the velocity in the crystal. The greater the facility of light transmission in the crystal the less is the difference from the more rapid transmission in air and the smaller is the value of $\frac{V_a}{V_c}$; and the less V_c becomes the higher does the refractive index μ work out, so that μ varies inversely as V_c. The three refractive indices, the minimum, the intermediate, and the maximum, for the rays vibrating respectively along OA, OB, and OC being indicated respectively by α, β, and γ in accordance with the usual convention, then OA or $\mathfrak{a}$ is thus proportional, as already shown, to $\frac{1}{\alpha}$, OB or $\mathfrak{b}$ to $\frac{1}{\beta}$, and OC or $\mathfrak{c}$ to $\frac{1}{\gamma}$. The two rays which can travel along OA, vibrating perpendicularly to each other parallel to OB and OC, will afford the two indices β and γ; similarly, the two rays that can travel along OB and which will vibrate parallel to OA and OC, will afford α and γ respectively; likewise, the two rays capable of passing along OC, will be composed of vibrations occurring along OA and OB respectively, and they will consequently afford the two indices α and β.

The double refraction is measured by the difference of the two extreme indices of refraction, $\gamma - \alpha$.

The Fresnel ellipsoid is thus defined by the meaning of its three rectangular principal axes and the three mutually perpendicular axial planes containing them, and this is all that is required for our practical work in determining the optical constants. But the ellipsoid has further important general properties, which at once express the behaviour of light waves transversing any direction in the crystal.

If OP in Fig. 649 be any direction whatsoever in the crystal and its Fresnel vibration-velocity ellipsoid, and if a section-plane perpendicular to it be taken through the crystal, the section of the ellipsoid by this plane being an ellipse, and if further the major and minor axes of the latter be OL and OM, then OL and OM represent the directions of vibration and the velocities of the two plane-polarised rays which can travel through the crystal along OP. The planes of polarisation of the two rays are at right angles to each other, the major and minor axes of the ellipse being mutually perpendicular. This is the fundamental law of double refraction.

The meaning of double refraction will now be quite clear. For it must be obvious that the two rays which can travel along any general direction such as OP, having two different velocities and therefore two different indices of refraction, must have been differently refracted on entering the crystal, that is, their previous paths in the air must have been different. If, therefore, we imagine these two incident rays, at first passing through the air inclined to each other, to close up their angle of inclination until they become identical as regards their direction through the air, their directions on entering the crystal must diverge again. Hence, a bundle of parallel rays derived from the same source must, when incident upon a crystal surface, become divided into two rays on entering the crystal substance, which in general traverse that substance in two more or less inclined directions according to the difference of their corresponding velocities and refractive indices, and the planes of polarisation and directions of vibration of which are perpendicular to each other. In the special case when the bundle is incident parallel to one of the three rectangular axes of the ellipsoid, the two rays into which it breaks up do not diverge, but both continue along the axis, with different velocities, however, and oppositely (rectangularly) polarised.

The major and minor axes of the elliptic section of the Fresnel ellipsoid by any perfectly general plane are termed " singular directions." In the special cases of the circular section of the ellipsoid of revolution of a uniaxial crystal, and the pair of circular sections of a biaxial crystal, every direction in such circular section is equivalent to a singular direction, there being no double refraction. Now there is usually some difficulty in understanding why a ray entering a doubly refractive crystal breaks up into two others only, and why these two should so conveniently vibrate perpendicularly to each other. The reason is that when a vibratory displacement occurs in any direction in the front of a wave it is only those components which are parallel to the singular directions (axes of elliptic section) which are propagated permanently as waves, and their propagation occurs with different velocities, except when the elliptic section becomes a circular section. This fact, which has been proved both experimentally and as the result of profound mathematical analysis, fully accounts for the bifurcation of the ray into two, and two only, perpendicularly vibrating components on entering the crystal.

It must be remembered also that in air the wave-front is perpendicular to the direction of a beam of light, but that in the crystal in general the wave-front is more or less inclined from the perpendicular to the direction of propagation, and that the inclinations of the two wave-fronts of the two bifurcated rays in the crystal, to the respective directions of propagation of those rays, are in general different. Similarly two rays travelling along the same path through a crystal and vibrating perpendicularly to each other, but with wave-fronts differently inclined as a rule, on emergence into air bifurcate as two differently refracted rays but with wave-fronts now perpendicular to each of the two different

directions of propagation. These facts will be made quite clear on reference to Fig. 650.

In all the above cases it must be understood that the ray or rays referred to are homogeneous monochromatic ones of definite wave-length, for both the velocity and the direction in general differ with the wave-length.

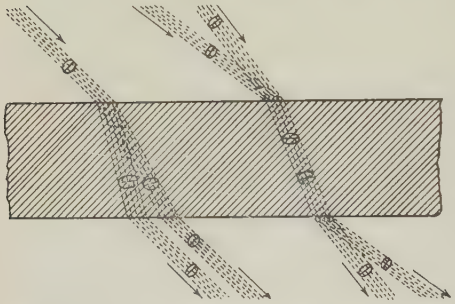


FIG. 650.—Diagram illustrating Different Inclinations of Wave-fronts of two Rays traversing Crystal.

It must be borne in mind that the wave-front of a beam of light traversing a cubic crystal or other isotropic substance such as glass is perpendicular to the direction of the beam, as in air, and when the beam is cylindrical the plane section formed by the wave-front is a circle. We have just seen, however, that in a doubly refracting crystal the wave-front is in general inclined out of true perpendicularity to the direction of propagation, and the section of the beam by the wave-front will therefore be an ellipse, which will be of different axial dimensions for the two differently refracted bifurcated rays, owing to the different inclinations of the sections to the directions. In the special case, however, of a beam travelling in a crystal along any one of the three axes OA, OB, OC of the optical ellipsoid its wave-front is actually perpendicular to the direction of propagation.

The Fletcher Indicatrix.—The fundamental fact of Fletcher's generalisation [1] is stated by him in the following words :

"The characters of a ray of plane-polarised homogeneous light transmitted within a (crystal) medium are indicated by geometrical characters at a corresponding point on an ellipsoid ; the direction of the ray is that of a diameter intersecting perpendicularly the normal drawn to the ellipsoid at the corresponding point ; the velocity is inversely proportional to the length of the normal intercepted by the ray ; the plane of polarisation is perpendicular to the normal."

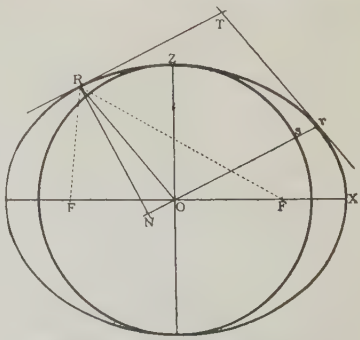


FIG. 651.—Diagram illustrating the Properties of the Indicatrix.

We may illustrate these properties of the indicatrix most clearly by considering first the special case of uniaxial crystals. Let us reproduce in Fig. 651 the wave-surfaces of a negative uniaxial crystal such as calcite, as given in Fig. 619, and draw any radius O*r* of the elliptic section of the extraordinary wave-surface, also *r*T the tangent at the

[1] *Mineralogical Magazine*, 1891, *9*, 278.

point r, and OR a line parallel to it. Then the tangent RT at the point R is parallel to Or, and OR and Or are thus conjugate semi-diameters of the ellipse, so that, in accordance with a well-known property of conjugate radii of the ellipse, the parallelogram ORTr is constant and equal to the parallelogram on the semi-axes OX . OZ. If now a perpendicular to the ellipse be drawn at R (that is, a line at right angles to the tangent RT), to meet the radius Or produced at N, the parallelogram Or . RN is also equal to OX . OZ (Euclid i. 35). If the value of this rectangle be taken as unity :

$$\mathrm{O}r = \frac{\mathrm{OX} \cdot \mathrm{OZ}}{\mathrm{RN}} = \frac{1}{\mathrm{RN}}$$

Hence, the velocity of propagation of any extraordinary ray, expressed by the length Or, is inversely proportional to the length of the straight line which at the point R is perpendicular both to the ellipse (and the spheroid) and to the ray. This straight line RN is the vibration-direction of the ray Or, for the plane of polarisation of the latter is that containing the propagation-direction Or itself and the perpendicular to the section (that is, to the paper).

This is precisely what is implied in the above-quoted statement of Fletcher. For the point R obviously determines both the direction and velocity of propagation, and the directions of vibration and of polarisation of a specific ray corresponding to the point. The point being a general one, that is, capable of being chosen anywhere on the ellipsoid, these geometrical characters at the point define the optical behaviour of any ray travelling within a crystal of uniaxial optical character absolutely. It is only necessary to draw the normal to the surface of the ellipsoid at the point in question, that is, to draw the perpendicular to the tangent at the point (the usual method being to bisect the angle between the lines joining the point and the foci F of the ellipse, the bisecting line being the normal), and then to draw a perpendicular to this to pass through the centre and produce it far enough to meet the ellipse again at r.

Besides RN there will be another normal to the radius vector Or, perpendicular to the plane of the paper at O, and lying in the equatorial circular section, with length equal to OX. It is related to the ordinary ray Os as RN is to the extraordinary Or, for it is the direction of vibration of the ordinary ray just as RN is the direction of vibration of the extraordinary ray, and the velocity of this ordinary ray is inversely proportional to OX.

Thus the relations of the ordinary and extraordinary rays in any direction in a uniaxial crystal can be derived from a single surface, an ellipsoid of revolution, the " indicatrix " or " indexellipsoid," the axis of rotation and the diameter of the equatorial circular section of which behave to each other as do the reciprocals of the velocities of propagation of rays vibrating parallel to and perpendicular to the axis, that is, as the two refractive indices ϵ and ω. For a negative uniaxial crystal, for which

$\omega > \epsilon$, its rotation axis is the smaller, and for a positive one, when $\epsilon > \omega$, the maximum axis is that of revolution.

The above derivation of the indicatrix of a uniaxial crystal is only that of a special case of the general ellipsoid of three axes proportional to the three refractive indices. In this general ellipsoid only the normals to its surface at the six points forming the ends of the three axes pass through the centre. To each of these points there correspond an infinite number of ordinary rays of equal velocity, and the directions of vibration of which lie in the perpendicular principal section-plane. But only three principal sections now occur, instead of the infinite number of such in the uniaxial ellipsoid, namely, those perpendicular to the three principal axes. As the propagation-velocity of the ordinary ray in such a principal section is inversely proportional to the semi-axis perpendicular to it, the length of which is each time different, the rays possess in each principal section a different refractive index. These three indices are the three chief ones α, β, γ, which thus correspond to three kinds of ordinary rays vibrating respectively parallel to the three principal axes.

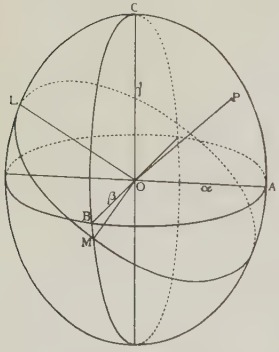


FIG. 652.
The Indicatrix of Fletcher.

We can at once construct the "indicatrix" of Fletcher from the three refractive indices α, β, γ determined experimentally for the three axial directions, which latter are common, of course, to the two ellipsoids of Fresnel and Fletcher, and which directions are known either from the morphological symmetry if rhombic, or from experimental determinations by the method of extinctions if the symmetry be monoclinic or triclinic. To construct the Fletcher indicatrix we take the length of the axis OA proportional to the minimum refractive index α, that of OB to the intermediate index β, and that of OC to the maximum index γ, as in Fig. 652.

There are three properties of practical importance possessed by the indicatrix:

(1) The principal axes OL and OM of any section of the ellipsoid—which as in the case of the Fresnel ellipsoid is always an ellipse except in the two special cases of the circular sections perpendicular to the optic axes—are proportional to the refractive indices of the two beams of light the **wave-directions** of which are parallel to the normal to the section OP, and not in general to those of the beams the directions of propagation of which within the crystal are parallel to OP itself. For these wave-directions are the perpendiculars to the wave-fronts, and are only identical with the directions of the rays when the latter both move along one of the three axes OA, OB, OC, that is, when the section is a principal one.

(2) As the principal axes OL and OM of the elliptic section lie in the planes containing the normal OP and the directions of vibration of the two plane-polarised beams, they (the axes) express the refractive

indices corresponding to the two beams and also their planes of polarisation.

(3) The difference in length of the two axes OL and OM affords the measure of the double refraction of the section-plate, that is, the bi-refringence along the direction of the normal OP.

Optic Axes and Median Lines.—The phenomenon of optic axes, so important in practical crystallography, is at once elucidated by the properties of the Fresnel ellipsoid or the indicatrix. It has already been pointed out that the ellipsoid of three unequal rectangular axes, which most generally represents the optical characters of crystals, must of necessity have a pair of circular sections, in certain positions which are dependent on the relations of the lengths of the three axes, but which will in any case be symmetrical to the principal elliptic section, the major and minor axes of which are the maximum and minimum axes of the whole ellipsoid.

For if we examine this principal elliptic section it will be obvious that, between these two extreme radii, in every quadrant of the ellipse there must be a position on the curve where if a radius be drawn to the centre it will be equal to the intermediate axis of the ellipsoid, the normal to the plane of the principal section under consideration. Hence, the section containing these two mutually perpendicular equal radii must be a circle. As the four points in question on the principal ellipse are symmetrically placed with respect to the maximum and minimum axes, they will lie at the ends of two diameters equally inclined to these principal axes, that is, opposite pairs of the four radii are in the same straight line ; and the two sections of the ellipsoid, each containing one of these two diameters and the intermediate axis of the ellipsoid perpendicular to them, will be the two circular sections in question which intersect in the intermediate axis.

Now the two normals to these two circular sections of the ellipsoid of general form will clearly be directions of single refraction. For rays transmitted along them will vibrate with equal velocity in all azimuths in the circular section perpendicular to the direction of the rays. These normals to the circular sections are the **" optic axes."**

This accounts for the fact that crystals of the rhombic, monoclinic, and triclinic systems of symmetry are " biaxial " ; for these are the systems the optical characters of which are expressed by an ellipsoid of general form.

When two of the axes of the general ellipsoid approach each other in length until they become equal, and the ellipsoid becomes one of revolution, the two circular sections rotate equally about their common diameter, the intermediate axis, until, when the latter becomes equal to the other axis the length of which it is approaching, the angle between the section-planes becomes zero and the two sections coincide, merging into a single circular section, perpendicular to the one principal axis, which remains different to the two now equal lying in the circular section. This outstanding axis perpendicular to the unique circular section is then the only one direction in the crystal along which no double refraction

occurs, and the crystal is consequently optically "uniaxial." Thus it is that crystals of the trigonal, tetragonal, and hexagonal systems of symmetry are characterised optically by an ellipsoid of revolution, the axis of which is coincident with the unique trigonal, tetragonal, or hexagonal axis of morphological symmetry, and that they display only a single optic axis, also identical with this same singular direction.

In the case of the optic axis of a uniaxial crystal this direction is truly and absolutely a direction of no double refraction, for rays transmitted along it are free to vibrate in any azimuth perpendicular to it, and do so with absolutely the same velocity in the directions of all the radii of the circular section perpendicular to the axis. Moreover, the wave-front of such a ray is always perpendicular to the direction of propagation of the ray, that is, a tangent to the wave-front is parallel to the circular section; the section of the cylindrical beam of rays itself is also circular and perpendicular to the ray-direction. Further, all rays travelling along the optic axis are ordinary rays, and afford the refractive index ω, corresponding to vibrations in the circular section.

The matter is not so simple as regards the two optic axes of a biaxial crystal, for the two circular sections are not like the uniaxial circular section in being each a principal plane of the ellipsoid; they are merely two ordinary sections of the ellipsoid by two planes symmetrically inclined to one of the principal planes, and intersecting in one of the principal axes of the ellipsoid, the intermediate axis. Hence, the wave-front of a ray travelling along either of the two optic axes of a biaxial crystal, perpendicular to one of these circular sections, will not be perpendicular to the direction of the ray, and the section of the cylindrical beam by the wave-front will have an elliptic and not a circular form. For it has already been shown (page 876) that a perpendicular wave-front affording a circular section of the beam only happens for a biaxial crystal when the ray is propagated along one of the three principal axes. The direction of vibration, however, will, as always, be perpendicular to the direction of the ray, and its plane of polarisation will be perpendicular to the direction of vibration and parallel to the direction of the ray. The inclination of the wave-front to the ray-direction, however, introduces a distinction from a uniaxial optic axis, and although its practical effect is so small that in most cases it is not detected by the ordinary experimental method of locating an optic axis, by means of the interference figure in convergent polarised light, still there are exceptional cases in which it becomes of practical importance, and it is necessary that the real nature of the case should be thoroughly understood. The question must, therefore, be investigated a little more closely.

Let the circular sections of both the indicatrix and the Fresnel ellipsoid be drawn, as in Figs. 653 and 654, and let their normals be N and N′, and n and n', respectively. As all the radii of the circular section are equal, and in the case of the indicatrix correspond to the refractive index for rays the wave-fronts of which are perpendicular to ON or ON′, it follows that all rays having these wave-fronts have the same refractive index corresponding to a velocity which is inversely propor-

tional to this index and to the radius OB which represents it graphically. Hence, these rays may be polarised in any plane and will not be resolved into two rays of definite planes of polarisation, and in short behave as if the crystal were singly refractive along these two directions of the normals ON and ON′. These directions are called the **"primary optic axes,"** and by Fletcher more precisely the **"optic binormals."**

But in the case of the Fresnel ellipsoid, the velocity along any direction is given by the axes of the section perpendicular to it, so that the rays passing along the normals O*n* and O*n′* to the circular sections can only have one velocity, the sections being circles and not ellipses. Hence O*n* and O*n′* are called the **"secondary optic axes."** The distinction must be remembered that it is here in the Fresnel ellipsoid a question of the ray itself travelling along the normal O*n* or O*n′*, and with a wave-front which may be slightly inclined from the perpendicular to

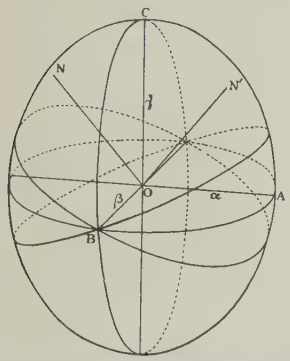


FIG. 653.—Fletcher Indicatrix showing the Primary Optic Axes ON and ON′.

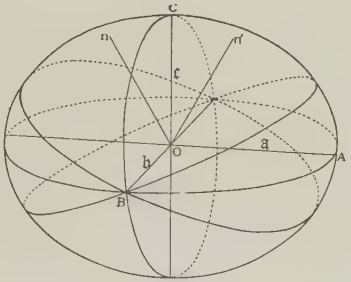


FIG. 654.—Fresnel Ellipsoid showing Secondary Optic Axes O*n* and O*n′*.

the direction of propagation; whereas, in the case of the indicatrix, it was the wave-front which was perpendicular to the direction ON or ON′ and was represented by the circular section, as this was the tangent plane of wave-fronts perpendicular to the binormal. The cases are not similar, because, as regards the case of the Fresnel ellipsoid, two rays may pass in the same direction inside a crystal having different wave-fronts, and also, as concerns the case of the indicatrix, rays having the same direction of wave-front may take slightly different paths through the crystal, that is, their paths may be slightly inclined to ON or ON′.

From the practical point of view, however, this distinction between primary and secondary optic axes is of little importance, for most rays are so nearly perpendicular to their wave-fronts that these two kinds of optic axes appear identical to all practical tests, except such as are specially designed to bring out such a minute difference. For even their accurately determined positions are rarely more than a very few minutes apart. Occasionally, however, exceptions are observed—sulphur, for instance, for which their separation amounts to $3\frac{1}{2}°$—so that the phenomenon cannot be ignored.

The observed optic axis, either of the two which are indicated in convergent polarised light by the vertices of the two hyperbolic "brushes" in the centres of the innermost optic axial interference rings, is really the axis of a cone of rays of very small angle, passing through the crystal and emerging in air as a cylinder. Those rays the paths of which inside the crystal lie on the surface of this cone are those which alone are singly refracted, and which unite on emergence to form the cylindrical beam. Within the cone, double refraction of a kind known as "Inner Conical Refraction" occurs. Hence, the two optic axes of a biaxial crystal are not entirely of the same character as the single optic axis of a uniaxial crystal. For the unique optic axis of the latter combines in itself the qualities of both primary and secondary optic axes, the two absolutely coinciding. Hence, the singular crystallographic axis of a trigonal, tetragonal, or hexagonal crystal is truly, in the strictest sense, a direction of no double refraction. For both the indicatrix and the Fresnel ellipsoid obviously become equally an ellipsoid of revolution in the cases of uniaxial crystals.

The nature of the **Cone of Inner Conical Refraction** can be best understood by considering the wave-surface. Let OA and OC in Fig. 655 be the axes of maximum and minimum vibration-velocity of the Fresnel ellipsoid, that is, the major and minor axes of the principal elliptic section. A ray propagated in air along the direction OA would, when travelling inside the crystal, outwards from the centre O towards A, be resolved into two rays vibrating respectively along OC (the direction of minimum vibration-velocity) and OB (perpendicular to the plane of the paper), the direction of intermediate vibration-velocity. When the latter ray had reached *b* the former would only be at *c*. Similarly, rays travelling along OC would be resolved into two inside the crystal, vibrating severally parallel to OA (the direction of maximum vibration-velocity) and to OB again (the intermediate vibration-velocity direction normal to the paper). Consequently, the former ray would have reached *a* when the latter had only reached *b'*. The two positions *b* and *b'* being equidistant from the centre, the section parallel to the paper, of the wave-surface of all rays vibrating parallel to the intermediate axis

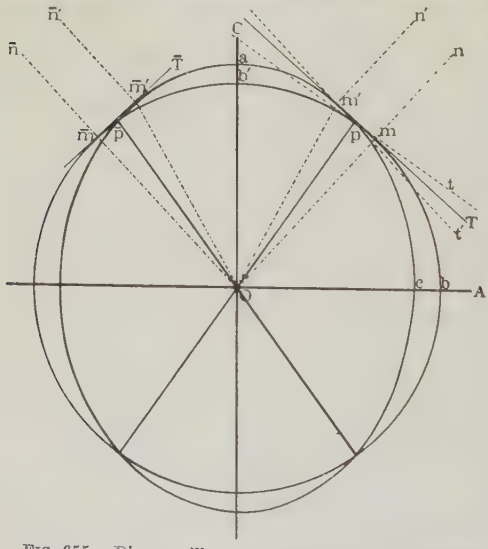


FIG. 655.—Diagram illustrating the Nature of the Cone of Inner Conical Refraction.

perpendicular to the paper, is obviously a circle, the radius of which is proportional to the intermediate vibration-velocity. The other curve on which a and c are situated, representing the wave-surface of waves vibrating in the plane of the paper, is an ellipse, with axes Oa and Oc proportional to the maximum and minimum vibration-velocities.

Rays travelling along the line joining the centre O and a point of intersection p of the circle and ellipse would travel with the same velocity within the crystal, because here the vibration-velocity is the same both perpendicular to and in the plane of the paper. These directions Op and $O\bar{p}$ are the "**Secondary Optic Axes,**" or "**Axes of Single Ray Velocity.**" But the tangents t and t' to the two curves at the point p are obviously differently inclined to Op, and the two rays travelling along Op will consequently be dissimilarly refracted on emergence into air. The two curves, however, have a common tangent T, and as similar arguments apply for rays travelling along OB (perpendicular to the paper) to those which have been used regarding waves propagated along OA and OC, the two curves in Fig. 655 are, as just indicated, really the sections of the two shells of the wave-surface, so that the common tangent T to the two curves is a plan or trace of a common tangent plane to the exterior shell, covering the depression in the latter, and the line of contact of which, as indicated in Fig. 642 illustrating the two shells of the wave-surface, is a small circle on which m and m' are two points, this circle being the base of the cone of inner conical refraction mOm'. All rays travelling within the crystal from the centre along the surface of this cone will consequently emerge as a cylindrical beam nn', parallel to the primary optic axis or the "optic axis" as measured by the use of the interference figure in convergent polarised light. The normal mn to the common tangent at the point m where it touches the circle is obviously a continuation of the radius Om at the point, and is the actual direction of the primary optic axis, the cylindrical beam being not only parallel to it but bounded by it on one side in the plane of the section, the other boundary being the parallel line $m'n'$. This direction of the "**Primary Optic Axis**" Omn is also termed the "**Axis of Single-Wave Velocity,**" and is identical with the direction of the normal to the circular section of the optical indicatrix, this normal and its fellow on the other side of the bisectrix of the optic axial angle being the "**Binormals**" of Fletcher. These two cylinders of rays nn' and $\bar{n}\bar{n}'$, parallel to the symmetrical pair of primary optic axes, together form the equivalent in biaxial crystals of the single optic axis of uniaxial crystals. But that the two cases are different will be apparent from the fact that there is the inside of the cone to consider, if we desire to go into the ultimate details of the biaxial case. The conditions are grossly exaggerated in Fig. 655 for obvious reasons of clearness, the angle of the cone rarely reaching 2 degrees. If the ordinary case were drawn to scale the angle of the cone would be so small that the two lines Om and Om' would almost lie in contact throughout their length, with m, p, and m' approximately identical.

When a section-plate is cut out of the crystal perpendicularly to the primary optic axis O*mn*, and a cylindrical beam of parallel rays is allowed to fall normally upon it, they will travel within the crystal along the surface of the cone, a circumstance from which the term **" Cone of Inner Conical Refraction "** takes its origin.

The above explanation is due to Sir William Hamilton,[1] and its correctness was proved experimentally by Dr. Humphrey Lloyd [2] in a memorable series of experiments suggested by the work of Sir William Hamilton. A crystal of aragonite was employed, the rhombic form of dimorphous carbonate of lime, $CaCO_3$. Aragonite, like the other better known trigonal form of calcium carbonate, our invaluable calcite, is a beautifully transparent colourless mineral very suitable for the purpose, and particularly so as it possesses a relatively large angle, nearly 2°, of inner conical refraction, combined with an unusually small optic axial angle, the true angle 2V*a* for sodium light being 18° 11′, and the apparent angle in air 2E being 30° 52′. The mode of carrying out the experiment is illustrated in Fig. 656.

A plate of aragonite *abcd* a quarter of an inch thick was ground out of a good crystal perpendicularly to the acute bisectrix of the optic axial angle, and a narrow beam of parallel light rays allowed to impinge on it from an aperture in a screen *s*. The surface of the plate nearest the screen was covered with a thin metallic plate *s′*, in which also a small aperture was pierced. The parallel beam was so arranged that it passed through the hole in the metallic plate, and was incident on the crystal at O at the semi-optic-axial angle in air, E = 15° 26′, as measured by the double of the angle of reflection *s*O*r*. The angles are all exaggerated in the drawing, as otherwise the cone of inner refraction would not be clearly visible. The rays then passed through the crystal along the surface of this cone of inner conical refraction O*mm′*, and the cylindrical beam was received on a silver screen *s″*. Two images of the aperture were produced on this screen *s″* until the adjustment of the plate and of both screens *s* and *s″* was perfectly attained, when suddenly the two images closed up and formed a brilliant ring of light, of unchanging diameter *nn′*, dependent only on the thickness of the plate. This remarkable result proved that the beam was indeed cylindrical and hollow, and that it corresponded to the light rays proceeding within the crystal along the surface of the cone. The angle of the cone was found to be 1° 50′, extremely close to the value, 1° 55′, predicted by Sir William Hamilton.

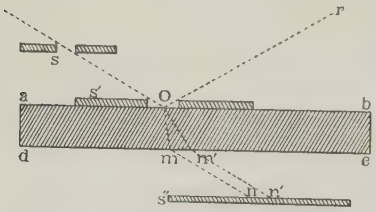


FIG. 656.—Lloyd's Experiment on Inner Conical Refraction of Aragonite.

It is also interesting to observe what occurs when a beam of light traverses the crystal along the direction of one of the secondary optic axes, say O*p* in Fig. 655. Such a narrow beam of parallel rays should emerge into the air as a conical beam, and does as a matter of fact, giving rise to the phenomenon of **" Outer Conical Refraction."** This was proved by a second experiment of Dr. Lloyd, employing the same

[1] *Dublin Transactions*, 1839, *17*, 132, an account of a paper read in 1832.
[2] *Phil. Mag.*, 1833, *2*, 112 and 207.

crystal plate of aragonite, *abcd* in Fig. 657, as for the experiment just described.

A metal plate perforated by a small hole was laid in this case against each surface of the crystal plate, and the two plates s and s' were so adjusted that the direction of the line through the crystal joining the two apertures was parallel to the secondary optic axis Op. A lamp flame was then adjusted on the O-side so that the axis of the cone of rays from it to the aperture at O made an angle of incidence of about 15½° on the plate, the amount of the semi-optic-axial angle. On looking from the other side through the aperture p in the plate s', the final adjustments having been carefully made, a bright ring of light was again seen. The cone of outer conical refraction *pqr* had been actually produced, and its basal circle afforded the brilliantly illuminated ring of light observed. On either side of this adjusted position the ring broke up into two images of the flame or aperture O. A similar ring of light was produced when the lamp was replaced by a beam of light focussed on the aperture O by means of a lens l, as shown in Fig. 657, so that the axis of the cone proceeding from the lens to the plate was a continuation of the line Op, the aperture at p cutting off all but this axial ray Op. The aperture p requires to be very small in this form of the experiment.

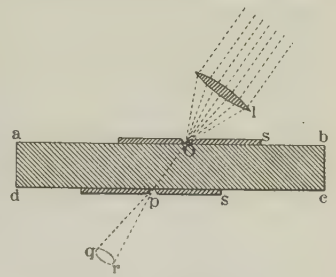


FIG. 657.—Lloyd's Experiment on Outer Conical Refraction of Aragonite.

The foregoing hitherto generally accepted explanations of the experiments of Dr. Lloyd have been shown by W. Voigt[1] not to express the whole truth. For the rays assumed to be parallel, as they fall on the crystal plate in the experiment for inner conical refraction, never are so truly and absolutely, a fact which is indicated by the observed gradual spreading out of the rays as they approach the hollow cylinder, instead of suddenly producing the bright ring. So long ago as the year 1839 it was observed by Poggendorff,[2] and confirmed later by Haidinger,[3] that when the pencil of rays is very fine the bright ring is divided by a dark circle into an inner and an outer ring. The investigation of Voigt in 1905 was directed to ascertaining the directions of the wave-normals closely adjacent to the optic binormals. When the wave-normal directions encircle the binormal, standing out at a small angular distance therefrom, the two sets of rays describe two cones, which are coaxial with the theoretical ray-cone of inner conical refraction, and the section of which perpendicular to the binormal consists of two concentric circles about equidistant from the circular section of the cone of conical refraction. All incident light-waves the normals of which fill the space between the two cones furnish consequently two concentric narrow rings of light. The light energy is the smaller the more minute the angle of the cone, and is a minimum, infinitely small, for that ring which originates from the infinitely narrow wave-normal cone which contains the binormal itself. Consequently the observed rings of light, the diameter of which depends on the angular aperture of the pencil of incident rays, correspond to

[1] *Phys. Zeitschr.*, 1905, *6*, 673 and 818. [2] *Annalen*, 1839, *48*, 461.
[3] *Ibid.*, 1853, *86*, 486.

wave-normals that are not exactly parallel to the binormal, and do not, therefore, originate from the conical refraction. As the size of the aperture increases, through which the light waves are admitted, the Poggendorff dark circle becomes invaded, irradiated, and eventually fully illuminated, by the mutually approaching and finally coalescing pair of bright rings, just as the two sodium D-lines of the spectrum become a single line when the very fine slit of a spectroscope is slightly opened out. As regards outer conical refraction, the distribution of intensity in the issuing cone of rays is essentially the same as in the incident rays, and there is no occasion, therefore, for the production of a dark ring analogous to that of Poggendorff. Yet here again the observed ring of light does not come from rays which have really suffered conical refraction and been transmitted exactly parallel to the axis of the rays, but from rays which have been transmitted along all possible other neighbouring directions closely adjacent to that axis.

The phenomena of internal and external conical refraction can be observed with the microscope by a method which has been described by R. S. Clay.[1] A crystal of aragonite is arranged on the microscope stage, and the microscope is arranged to afford the interference figure in convergent polarised light, as described in Chapter LII. The crystal plate is then tilted until one of the optic axes is brought to the centre of the field, so that this optic axis becomes parallel to the axis of the microscope. A thin brass plate pierced by a pinhole has previously been placed under the crystal plate closely in contact with the latter, and with the pinhole central. A second similar brass plate pierced by a somewhat larger pinhole, not exceeding half a millimetre in aperture, however, is also arranged beneath the stage, say in or on the condenser tube from which the lenses have been removed (or otherwise supported at about the distance from the stage which the condenser usually occupies). The light from a sodium flame is then reflected by the mirror through the larger pinhole and towards the smaller one. The microscope is now arranged for parallel light, a lower power objective being employed than was used for producing the interference figure, and the upper surface of the crystal is focussed. Two dots then become visible, and on moving the lower pinhole diaphragm about in its own plane the two dots alter their position, and this alteration occurs more and more rapidly the more correctly the optic axis has been adjusted parallel to the microscope axis; when the adjustment of the diaphragm has also been correctly obtained for the observation of the desired phenomenon the two dots rotate rapidly around one another, and with a little final adjustment they eventually suddenly enlarge into a continuous circle of light. That this ring of light is the section of a cylinder is proved by gradually raising the microscope by the coarse adjustment so as to focus sections of the cylinder at different distances from the crystal, when it is found that the ring remains approximately of the same size.

The experiment can be made quantitative by measuring the diameter of the ring, with the aid of a calibrated micrometer eyepiece, and also

[1] *Treatise on Practical Light*, p. 481.

measuring the thickness of the crystal plate with the thickness measurer (Fig. 893 on page 1320 in Chapter LVII.). The former dimension (the diameter of the circular base of the cone) being lettered AB, and the latter (lying on the cone) being either AC or BC, when ABC is the triangle representing the cone, the angle of the cone ACB can be calculated, and for aragonite will work out 1° 55′.

A similar experiment can be carried out for the observation of external conical refraction, but the two pinhole diaphragms must be closely below and closely above the crystal, and carefully mutually adjusted until the two dots first seen move rapidly around each other and eventually open out into a circle. This is now the section of a cone and not of a cylinder, as it changes its size on raising the microscope. Measurements of its size at two different measured heights afford means of calculating the angle of the cone, which is 3° 1′ for aragonite.

The phenomena of inner and outer conical refraction thus afford the final proof that the theory of the transmission of light through biaxial crystals given in this chapter is correct, and also demonstrate in the most perfect manner the true character of the two optic axes of a biaxial crystal, and their essential difference from the simpler single optic axis of a uniaxial crystal.

The Median Lines, and their Order with respect to the Refractive Indices.—Whichever one of the two extreme axes, the maximum and minimum axes, of the optical ellipsoid (whether the latter be the indicatrix or the Fresnel ellipsoid) bisects the acute angle between the two optic axes, is termed the **"First Median Line"** or the **"Acute Bisectrix of the Optic Axial Angle."** The other of these two axes is then obviously the **"Obtuse Bisectrix of the Optic Axial Angle"** or **"Second Median Line."** Considering the indicatrix as the more practical ellipsoid for our purpose, as its axes directly represent the relations of the three refractive indices, if the intermediate axis, as represented relatively by its refractive index β, be nearer in relative length to the minimum axis as represented by the refractive index α, than to the maximum axis represented by γ, then the crystal is said to be a **"Positive"** biaxial crystal; but if β be nearer to γ than to α, then it is a **"Negative"** crystal. In the former case of a positive biaxial crystal, shown in Fig. 653, the circular sections will be inclined to the plane of the α and β axes at less than 45°, and their normals, the optic axes, will thus lie symmetrically at an angle of less than 45° on each side of the maximum axis γ, which is, therefore, the acute bisectrix or first median line, α being the obtuse bisectrix or second median line. This will be still clearer from a consideration of the simple Fig. 658. In the latter case of a negative crystal the converse happens, α being the first median line and γ the second, the circular sections lying less than 45° from the axis γ. A very useful fact to remember is that the first median line is always that extreme axis which is furthest in value from β.

In those systems, the monoclinic and triclinic, in which the orientation of the optical ellipsoid is not fixed by the symmetry (except that in the monoclinic system one of the axes of the ellipsoid is identical with the

symmetry axis), the median lines will differ in position (except that identical with the monoclinic symmetry axis, if such identity occur) for different wave-lengths of light and different temperatures; in other words, the median lines will show dispersion under different conditions. The various modes in which this can occur will be studied in detail in the latter part of the next chapter.

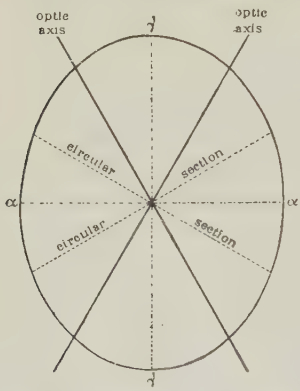


FIG. 658.—Disposition of Optic Axes in Positive Biaxial Crystal.

Résumé of Relations between Morphological Crystal Symmetry and the Optical Ellipsoid.

Uniaxial and isotropic crystals may be considered as special cases of the more general biaxial crystals. For when two of the principal axes of either the indicatrix or the Fresnel ellipsoid become equal, as in trigonal, tetragonal, and hexagonal crystals, an ellipsoid of revolution is produced, the crystal becoming optically uniaxial. The axis of revolution is then not only the principal crystallographic axis, the trigonal, tetragonal, or hexagonal axis in the crystals of these systems, but also the unique optic axis or direction of no double refraction. There will be only two refractive indices, now labelled ω (vibrations perpendicular to the axis) and ϵ (vibrations parallel to the axis) on account of the corresponding rays being ordinary and extraordinary; for two of the three refractive indices corresponding to the general biaxial case are now equal.

When all the axes of the ellipsoid are equal, the latter becomes a sphere, and we have the special case of cubic crystals, with no double refraction in any direction, the isotropic character being accompanied by the display of the highest type of morphological symmetry. All sections being circular, all rays will travel with equal velocity throughout the crystal, and there will be only one refractive index, now generally labelled μ as for isotropic substances in general.

The general case, that of a biaxial crystal, has been shown to apply to all orthorhombic, monoclinic, and triclinic crystals, the ellipsoid having three different rectangular principal axes, three different refractive indices α, β, γ, corresponding to rays vibrating parallel thereto, and two optic axes. The highest type of symmetry here involved, the orthorhombic, is characterised by identity of the three rectangular crystallographic axes with those of the optical ellipsoid, whether the latter be the indicatrix or that of Fresnel. In the monoclinic system, the ellipsoid is free to rotate about the unique axis of symmetry, which alone is identical in direction with one of the axes of the ellipsoid, which may be any one, but the particular one is definitely determinate for each substance crystallising in this system.

The position, as regards rotation about this axis, is definite within certain limits for each substance; but rotation does occur, indicated by dispersion of the two axes of the ellipsoid lying in the symmetry plane, for different wave-lengths of light and for different temperatures. In the triclinic system there are no restrictions as to the relative positions of the morphological and ellipsoidal axes, except, of course, that the three principal axes of the ellipsoid are, in accordance with the very nature of an ellipsoid and in contradistinction to the oblique relations of the crystallographic axes, at right angles to each other as always.

CHAPTER XLII

INTERFERENCE COLOURS OF THIN FILMS DUE TO TWO REFLECTIONS, AND INTERFERENCE PHENOMENA EXHIBITED BY CRYSTAL PLATES IN PARALLEL AND CONVERGENT POLARISED LIGHT, DUE TO DOUBLE REFRACTION

Newton's Rings and Orders of Colours.—One of the most familiar phenomena in optics is the production of Newton's spectrum-coloured rings by pressing two glass surfaces closely together. It will be remembered that they are best produced either by laying a plano-convex lens of very large radius of curvature by its convex side on a plate of glass, or by placing two circular plates of truly parallel and plane-surfaced glass together, with a marginal annulus of gold leaf between them, and pressing inwards the centre of one of the plates by a screw carried by the supporting annular frame, in order to cause the plates to touch at the centre. In either case the essential thing is a circular film of air the thickness of which increases regularly and excessively slowly from zero at the centre to a perceptible thickness at the circumference. The interference rings, iris-coloured in white light but sharper and black in monochromatic light, may be observed either by reflection or transmission. The former, as it affords the more brilliant spectacle, is usually preferred for demonstration purposes. The reflected and transmitted rings occupy complementary positions, the dark annular bands of the one in monochromatic light occupying the positions of the bright ones of the other Fig. 659, the

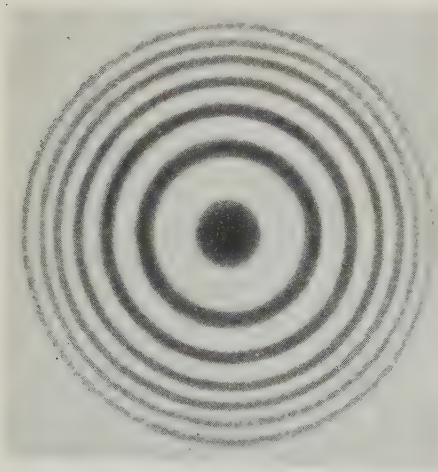


FIG. 659.—Photographic Reproduction of Newton's Rings as seen in White Light.

reproduction of a photograph of the rings in white light, will remind the reader of their appearance, as far as a photograph in black and white can do so ; and Fig. 660 will recall the conditions, the curvature of the curved surface being immensely exaggerated for the sake of clearness.

The rings are equal in area, hence they get narrower as we recede from the centre. When the incident ray enters, it is reflected both from the under surface AOB of the lens or bent plate, say at the point Q, and from the upper surface of the plate COD, say at P, and these two reflected rays will differ in phase according to the thickness PQ of the air-film at the spot, that is, according to the amount of extra path traversed by the ray reflected from the plane surface COD. When the delay is to the extent of half a wave-length, as shown on p. 800 of Chapter XXXVI. in discussing the subject of the interference of light-waves, total interference and mutual destruction should occur, half-phase difference always producing extinction of the light, assuming it to be strictly monochromatic, that is, composed of vibrations of a single wave-length. If the wave-length be varied, that is, if the apparatus be illuminated by monochromatic light of different colours in succession, the black rings will alter their position, both as regards their distance from the centre and their mutual distances from each other, becoming closer together or opening out according as the change is made towards the blue or the red end of the spectrum, that is, as the wave-length is shortened or increased. The radius of any ring varies as the square root of the wave-length of the light producing it. Consequently, in white light the dark rings produced for one constituent colour are illuminated by the bright rings of other colours, the most effective and predominant being the complementary colour. Hence, rainbow bands are produced, and each ring is bordered inside by red and outside with violet. After the seventh ring the further ones overlap one another so rapidly that they are invisible in white light, the ordinary effect of white light being afforded. The rings also change their position with alteration of the angle of incidence of the light.

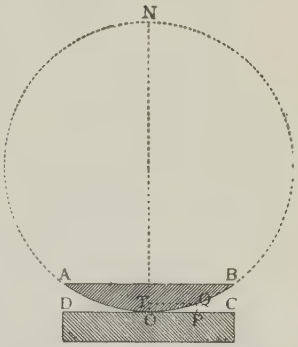


FIG. 660.—Conditions for the Production of Newton's Rings.

The order of the colours given by Newton as succeeding each other in the several rings produced in white light, starting from the centre, is as follows : **First** (central) ring, black (central spot), blue, white, yellow, red ; **second** ring, violet, blue, green, yellow, red ; **third** ring, purple, blue, green, yellow, red ; **fourth** ring, green, red ; **fifth** ring, greenish-blue, red ; **sixth** ring, greenish-blue, pale red ; **seventh** ring, greenish-blue, reddish-white. This succession of colours is universally known as "Newton's Scale of Colours," or "Newton's Seven Orders of Spectra." It is useful to remember it or to have ready access to it, so that we may be able to recognise the particular order to which any polarisation or

thin-film colour belongs. Red, in particular, is frequently referred to as " of the second order," " third order," or whatever order the colour under observation belongs to, meaning that it is the same quality of red as is seen in the second, third, or other ring of Newton's series of interference fringes.

Measurement of Thicknesses for, and Conditions for Production of, Newton's Rings.—An actual measurement by Schwerd of the thickness of the air-film at the position where the first bright ring in monochromatic red light is produced, surrounding the central black spot corresponding to contact, revealed the fact that it was about the 1/160,000th of an inch, which is approximately one-quarter of a wave-length of red light. For the exact wave-length of red C-hydrogen light is, in British measure, 1/38,710 inch, and that of the red ray of cadmium 1/39,459 inch.

Now the light rays have to traverse this thickness twice, so that the retardation is 1/80,000th of an inch. Hence, the first **bright** ring corresponds to a retardation of half a wave-length, which we usually associate with extinction. The explanation is a curious and interesting one, namely, that the act of reflection of a light-wave in air at the surface of a denser medium, glass in this case, itself alters the phase by half a wave-length. It may be illustrated by the fact that when two particles of different mass collide, if it be the lighter which strikes the heavier the former will not only set the latter in some motion, but will also itself rebound and thus reverse its own motion. This sudden reversal corresponds, in the case of ether particles producing waves of light, to a retardation or acceleration of half a wave-length, $\lambda/2$, that is, to a reversal of phase, on passing from a lighter to a denser medium. If, on the contrary, the heavier particle strike the lighter it continues its direction of motion, carrying along with it the latter, so that no change of phase occurs when light passes from a denser to a rarer medium.

Hence, in the Newton's rings experiment there is no change of phase at the curved upper surface of the two surfaces concerned in the interference, but only at the plane lower surface. Consequently, there is only one such change of phase of $\lambda/2$, which is, therefore, the total retardation due to reflection which requires to be added to that due to the difference of path. Thus it comes about that we have a bright ring at the position where the difference of path alone would correspond to a dark ring, and at the centre, where the difference of path is zero, there being contact, the half wave-length change of phase due to reflection alone operates, the ensuing extinction accounting for the black central spot.

Newton, in a series of experiments with yellow light, found the absolute thicknesses of the film corresponding to successive dark rings to be 2/178,000, 4/178,000 inch, and so on, when the incidence was 4°. This gives 1/44,500 inch for the wave-length of yellow light, which is interesting as being the first determination of the wave-length of a light radiation, although Newton himself did not recognise the fact.

Each dark ring thus corresponds to a further difference of path (twice the difference of thickness, as the space is traversed twice) of a whole wave-length, the additional half wave-length due to reflection

being constant throughout. The difference of thickness of the air-film for each successive dark ring is thus half a wave-length. These facts will be clear from the following table, which shows the thicknesses and retardations for each dark and bright ring in their regular order, as far as the third in each case, starting from the centre:

CONDITIONS FOR PRODUCTION OF NEWTON'S RINGS.

Order of Ring.	Thickness of Air-film.	Retardation.				
		Due to Difference of Path.		Due to Reflection.		Total.
Central black spot .	Zero	0	+	$\frac{\lambda}{2}$	=	$\frac{\lambda}{2}$
First bright ring . .	$\frac{\lambda}{4}$	$\frac{\lambda}{2}$	+	$\frac{\lambda}{2}$	=	λ
First dark ring . .	$\frac{\lambda}{2}$	λ	+	$\frac{\lambda}{2}$	=	$1\frac{1}{2}\lambda$
Second bright ring .	$\frac{3}{4}\lambda$	$\frac{3}{2}\lambda$	+	$\frac{\lambda}{2}$	=	2λ
Second dark ring .	λ	2λ	+	$\frac{\lambda}{2}$	=	$2\frac{1}{2}\lambda$
Third bright ring .	$\frac{5}{4}\lambda$	$\frac{5}{2}\lambda$	+	$\frac{\lambda}{2}$	=	3λ
Third dark ring . .	$\frac{3}{2}\lambda$	3λ	+	$\frac{\lambda}{2}$	=	$3\frac{1}{2}\lambda$

The thickness t of the film for the production of any dark ring, the radius r of the ring, and the radius of curvature R of the curved surface (of the lens or curved plate) are connected in the following manner by the two formulæ numbered (1) and (2), which can readily be elucidated from Fig. 660. If ON be that diameter of the circle of curvature of the lens which is normal to the plate, and a line TQ be drawn parallel to the plate from the point Q where the light is incident on the curved surface, so that $TQ = r$, and $OT = QP = t$, then, by a well-known property of the circle (Euclid, iii. 35):

$$(TQ)^2 = NT \cdot TO;$$

that is,

$$r^2 = NT \cdot t, \text{ or } t = \frac{r^2}{NT}.$$

But when R is very large NT may without sensible error be taken as equal to 2R, and it may certainly be so taken for a curved surface so nearly a true plane as is required for the production of Newton's rings; hence,

(1) $$t = \frac{r^2}{2R}.$$

Now it will be shown in the next section that the condition for interference (extinction) is:

$$t = \frac{n\lambda}{2\mu \cos \phi},$$

a formula which thus affords another expression for t, and in which λ is the wave-length in the medium of the film, in this case air, ϕ is the angle of incidence on the second surface relevant to the interference, n is the number of the ring taken consecutively from the centre, and μ is the refractive index of the material of the

film. As the latter in the case of Newton's rings is air, $\mu = 1$. Hence, for the production of the black ring n we must have :

$$(2) \qquad \frac{r^2}{2R} = \frac{n\lambda}{2 \cos \phi};$$

or, if r_n be the radius of the ring numbered n,

$$r^2{}_n = \frac{n \cdot \lambda \cdot R}{\cos \phi}.$$

When the incidence is normal $\phi = 0$, and $\cos \phi = 1$, so that the formulæ (1) and (2) simplify respectively as under, t_n being the thickness of the air-film at the place where the ring n is produced :

$$(1)\ t_n = n\frac{\lambda}{2}, \text{ and } (2)\ r^2{}_n = n\lambda R.$$

Hence the squares of the radii of the dark rings are proportional to n, which is represented by the natural numbers 1, 2, 3, 4, and so on. At the centre there is interference for all colours ; consequently, a black spot is produced.

Colours of Thin Films.—If a transparent parallel-surfaced plate be so thin that the retardation of the rays reflected from one surface, behind those reflected from the other surface, is so slight as to fall within the limits corresponding to the first seven rings of Newton, the whole plate will exhibit the particular colour to which such retardation corresponds in the case of the production of the rings. In Fig. 661 let ABCD represent such a film, say of blown glass, soap solution, or turpentine floating on water, and IP a ray incident at the angle θ on the upper surface APB of the film, where part is reflected and part refracted at the angle ϕ towards S. At the second surface CSD of the film reflection occurs again towards Q, and at Q also from the recovered first surface ; but here refraction also occurs, the refracted ray escaping towards R. But a directly reflected ray QR, incident at Q in the direction I'Q, will also reach the observer's eye together with this refracted ray QR derived from the internal reflection of the first ray IPS at S ; that is, two rays, one of which has traversed the film and the other has not, will reach the eye of an observer looking along the direction RQ. They will be in a position to interfere with each other if their difference of path should be approximately half a wave-length or an odd multiple of this, and the effect will be visible by the production of colour of one of Newton's orders when the retardation does not exceed the seven wave-lengths corresponding to the seventh ring. Their difference of path may be found in the following manner :

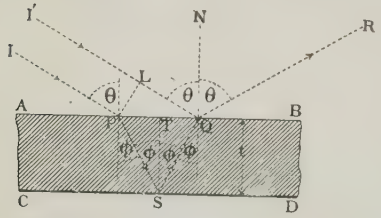


FIG. 661.—Diagram explanatory of Colours of Thin Films.

Draw PL perpendicular to IP and also the normals QN and TS to the two surfaces. Then the difference of path of the two rays is PS + SQ − LQ. Now PS + SQ = 2SQ, and if the thickness of the film be t :

$$(a) \qquad 2SQ = \frac{2ST}{\cos \varphi} = \frac{2t}{\cos \varphi}.$$

Also $LQ = PQ \cos LQP = PQ \sin \theta$, and $PQ = 2TQ = 2TS \tan \phi = 2t \,.\, \tan \phi$.

Hence, (*b*) $LQ = 2t \,.\, \sin \theta \tan \phi$.

But the part (*b*) of the path, LQ, is in air, while the part (*a*), PSQ, occurs in the film, the relative velocities being afforded by the ratio of the refractive index μ for the material of the film to that of air, which latter is unity. Hence, the value of (*a*), as the progress of this ray will be prolonged, must be multiplied by the refractive index of the film μ. We then have for the total difference of path d of the two rays:

$$d = (a) \,.\, \mu - (b) = \frac{2t\mu}{\cos \phi} - 2t \,.\, \sin \theta \tan \phi.$$

As $\mu = \dfrac{\sin \theta}{\sin \phi}$, and therefore $\sin \theta = \mu \sin \phi$, we may substitute this latter for $\sin \theta$ and thus obtain:

$$d = \frac{2t\mu}{\cos \phi} - 2t\mu \,.\, \sin \phi \tan \phi = 2t\mu \left(\frac{1}{\cos \phi} - \sin \phi \tan \phi \right)$$

$$= 2t\mu \left(\frac{1}{\cos \phi} - \frac{\sin^2 \phi}{\cos \phi} \right) = \frac{2t\mu}{\cos \phi} (1 - \sin^2 \phi) = \frac{2t\mu}{\cos \phi} \cos^2 \phi, \text{ that is,}$$

(*c*) $$d = 2t \,.\, \mu \,.\, \cos \phi.$$

Thus we arrive at the simple expression (*c*) for the difference of path d between the two rays proceeding together from any point of a thin film to an observer's eye, the one ray by direct reflection at the surface and the other having also traversed the film.

But there is a further consideration affecting the relative phases of the two, namely, as to what occurs at the limiting surfaces of the lighter air and the denser film. It has already been shown that a change of phase of $\lambda/2$ occurs at the limiting surface when a light-wave in air meets with a denser medium, and is reflected at the surface of the latter; while no such change of phase occurs when the conditions are inverted, the amplitude of the vibration only being affected without reversal of its direction. Hence, there is only one such change of phase of $\lambda/2$ due to the limiting surfaces, as in the case of Newton's rings, namely, on the part of the directly reflected ray I′QR. We have to add, therefore, to the difference of path d just found a further $\lambda/2$, which may be equally indifferently considered as a retardation or an augmentation, the interference effect of an exact half wave-length being the same for both, namely, conversion of light to darkness or *vice versa*. Hence, the total retardation of the penetrating ray behind the directly reflected ray is

$$2t\mu \cos \phi + \frac{\lambda}{2},$$

when t is the thickness of the film, μ its refractive index, ϕ the angle of incidence on the second surface of the film, and λ is the wave-length of the light in air.

When t becomes infinitely small the two waves will differ by the phase change of $\lambda/2$ alone, and extinction will occur, as at the central black spot in Newton's rings. It will be obvious that the film will dissipate, disrupt, or burst before this infinite thinness is attained, but just before it does so the brilliant colours give place to a dark grey, corresponding to just beyond the beginning of the first order of Newton's scale. Actual measurements of the thinnest soap films are very difficult

to carry out, but it is highly interesting that three black spots on a soap film were found by J. Perrin [1] to have thicknesses varying from 6 to 15 $\mu\mu$. The finest foam of soap solution is oily and acid, consisting of oleic acid produced by hydrolysis of the sodium oleate, and it has a thickness of only 2 $\mu\mu$ (=1/500,000 mm.). The film is probably, therefore, only 2 molecules thick, oleic acid $C_{18}H_{34}O_2$ being a substance containing a large number of atoms to the molecule.

Extinction will also occur if the total retardation be any odd number of half wave-lengths, that is, if

$$\text{Total retardation} = 2t\mu \cos \phi + \lambda/2 = (2n+1)\,\lambda/2,$$

or, simply, when

$$\text{Retardation due to difference of path} = 2t\mu \cos \phi = n\lambda.$$

That is, the thickness of the film for total interference, extinction, must be

$$t = \frac{n\lambda}{2\mu \cos \phi}.$$

It has been essential to render this condition for interference in thin films perfectly clear in order that we may thoroughly grasp the nature of the colours exhibited by doubly refractive crystal plates; for the retardation behind the other, of one of the two rays into which such a crystalline plate divides the light, gives rise to phenomena in polarised light of a similar character in many respects to the colour changes displayed in ordinary light by thin films of liquids or singly refractive transparent solids.

The fact will doubtless have been made apparent that a parallel-surfaced film merely affords over an extended surface the phenomenon of light, colour, or darkness (extinction) exhibited at any one annulus of equal thickness of the plano-concave lenticular film employed in producing Newton's rings. The consideration of these phenomena of ordinary light in a film of gradually varying thickness will also assist us greatly in understanding the important action of the quartz wedge in polarised light, to be studied later in this chapter.

Colours afforded by Crystal Plates in Parallel Polarised Light.—When a parallel-faced plate cut or ground out of a cubic crystal free from internal strain, or a naturally tabular crystal of this system, is examined between the crossed Nicol prisms of a polariscope, the rays being approximately parallel (that is, the special "converging system" of lenses usually provided with a polariscope not being used), it behaves like a plate of glass or other non-crystalline transparent isotropic substance. The field remains dark, and does so also when the crystal is rotated in its own plane. But if a similar plate belonging to a doubly refractive crystal, that is, one belonging to any other crystal system than the cubic, be examined and rotated in its own plane in the dark field, it will show light in certain positions of azimuth, unless, if it be uniaxial, it happens

[1] *Ann. de physique*, 1918 (ix.), *10*, 160.

to be a section cut perpendicularly to the optic axis or, if it be biaxial, it is normal to one of the two optic axes. The light will be white or coloured according to the relation between the thickness of the plate and the amount of the double refraction. **During a complete revolution of the plate in its own plane,** the polariscope being provided with a rotating stage, **the field of view will become four times light and four times dark, light and darkness succeeding each other alternately at equidistant intervals of 45°.** That is, the positions for darkness will be at right angles to each other, and fairly sharply defined, within half a degree of 90° 0′ even to an unpractised eye. **These positions of darkness occur in the case of a uniaxial crystal when the trace of that principal section of the optical ellipsoid of revolution which contains the normal to the plate becomes parallel to the plane of polarisation of either of the crossed Nicol prisms.** This is the law of Malus. **In the case of a biaxial crystal the extinction directions are parallel to the traces of the planes bisecting the angles between the two planes containing the two optic axes and the normal to the section.** This is the law of Biot. In the simple special case of a uniaxial crystal plate cut parallel to the axis, the extinctions occur whenever the direction of the optic axis is parallel to either of the vibration planes of the crossed Nicols; in the special case of a biaxial crystal plate cut perpendicularly to any one of the three principal axes of the optical ellipsoid, extinction occurs whenever the vibration directions of the Nicols are parallel to the other two axes of the ellipsoid to which the plate is parallel.

Whether the light which appears at the intermediate positions, the maximum intensity being at 45° from the positions of extinction, is white or coloured depends on the relation just referred to between the thickness and the double refraction. For the production of colour in ordinary light by a thin film is closely paralleled by the display of brilliant colour by crystal plates in polarised light. We have seen that in reflection from the two surfaces of a thin film one ray, that which penetrates to the second surface before reflection, is retarded behind the other, reflected directly from the first surface, by double the thickness of the film which it had twice to traverse, the interference thereby produced being the cause of the colour. In the case of a crystal plate, however, the interference is brought about by the retardation of one of the two rays, into which a doubly refracting crystal divides the light transmitted by it, behind the other, owing to the difference in velocity of the two rays, the path traversed not being necessarily different, although usually it is slightly so owing to different refraction being the accompaniment of different velocity.

When the doubly refracting crystal plate is of such a thickness that the retardation of one of the rays behind the other, due to both difference of velocity and difference of path, is such that the two rays emerge differing by a half wave-length, we naturally expect interference to occur, extinction if the light be monochromatic, but chromatic interference if white light be used, and assuming that the planes of polarisation are compatible with interference.

In reality, however, when we examine such a plate in the dark field of the polariscope—the planes of polarisation of the Nicols being thus crossed, and the plate being arranged as regards azimuth so that its directions of vibration (traces of principal sections of optical ellipsoid or of the Biot bisecting planes, the "extinction" positions) are at 45° to the planes of polarisation or vibration of the two Nicols, the positions for maximum transmission of light—we find that interference occurs when the two rays differ in phase by a *whole* wave-length, instead of by a half wave-length as expected. The fact is most clearly revealed in monochromatic light, for instead of the anticipated light of the colour used we get darkness when the difference of phase is one, two, three or up to seven, whole wave-lengths, the intermediate odd half wave-lengths of difference corresponding to the transmission of the coloured light. In white light we get brilliant colour instead of darkness for whole-wave retardation.

The reason for this reversal of our expectations is due to the fact that the Nicol analyser itself introduces, when crossed to the polarising Nicol, a change of phase of half a wave-length, like the act of reflection in the case of thin films, and this $\lambda/2$ requires to be added to the retardation of one ray behind the other brought about in traversing the crystal.

The polarising Nicol provides us with a beam of plane-polarised light, vibrating perpendicularly to the plane of polarisation of the Nicol. The latter was shown in Chapter XL. to be parallel to the longer diagonal of the end faces of the prism. Supposing this to be horizontal, the plane in which the vibrations occur (parallel to the shorter diagonal) will be vertical, assuming the light to be traversing the prism in the proper manner, parallel to the long edges of the rhomb, and that the polariscope is horizontally arranged. On now introducing a doubly refracting crystal plate, with its rectangular directions of vibration (parallel to two of the three axes of the indicatrix if the crystal be biaxial and the plate be cut perpendicularly to the third axis, or in general, those indicated by the laws of Malus and Biot) parallel and perpendicular respectively to the direction of vibration of the light leaving the polariser, the plane-polarised beam will obviously be transmitted, its vibrations being parallel to the former of the two possible planes of vibration in the crystal. The analysing Nicol will also clearly permit the beam to pass through to the observer or the screen, if it be also arranged with its plane of vibration parallel to the same direction, but will cut off the light altogether if crossed at right angles thereto. Thus the dark field afforded by the crossed Nicols alone is unaffected by the introduction of the crystal plate between them when the vibration directions of the rays possible to be transmitted by the crystal, in accordance with the law of Malus for a uniaxial crystal and that of Biot for a biaxial one, are parallel to the two rectangular vibration directions of the Nicols. This is the foundation of the "extinction" mode of determining the positions of the axes of the optical ellipsoid, which will be practically described in Chapter XLV., and as regards methods invoking the use of the polarising microscope, in Chapter LIII.

An excellent example of a doubly refracting crystal plate for verifying these facts, and those of the next few paragraphs, is a cleavage one of gypsum (selenite), known to opticians as an "even selenite." Thin plates, almost films, of this mineral afford particularly brilliant colours, owing to the beautifully transparent and colourless nature of selenite. The cleavage occurs parallel to the symmetry plane of the monoclinic crystal, so that the plate is perpendicular both to the crystallographic symmetry axis and to one of the axes of the optical ellipsoid, as will be more fully explained later in this chapter (see Fig. 662, p. 904). The other two rectangular axes of the ellipsoid consequently lie in the plane of the plate, and are the directions of "extinction." Two varieties are to be purchased, if it be not desired to cleave the necessary film for oneself (which, however, is advisable in order to gain the necessary most useful experience), namely, one which affords green and red complementary colours when the Nicols are parallel and crossed respectively and the selenite is placed with its planes of vibration at 45° to those of the Nicols, and another giving yellow and blue under the same conditions.

When we rotate the doubly refracting crystal plate between the crossed Nicols we observe thus four positions at 90° from each other in which the dark field is restored, the planes of vibration of crystal and Nicols being identical. At the intermediate 45° positions the maximum of light is observed to be transmitted, and less and less on each side as the 90° positions are approached. When the plate is thick the light is white, although it may be "white of the higher orders" of Newton when the thickness is not much greater than corresponds to the production of seventh order colours. But if the plate be thin enough, such as in the case of an "even selenite," to correspond to a retardation of anything under seven wave-lengths, colour is produced of the same type as one of Newton's orders, the particular colour depending on the thickness for any one substance. Thus, when a red-green even film of selenite is used the colour will be brilliant red with crossed Nicols and the plate at 45° to them, and if a blue-yellow film be employed a bright greenish-blue will be seen when the film is arranged at 45° to the crossed Nicols.

The α and γ axes of the indicatrix are the two which form the rectangular vibration directions of a cleavage plate of selenite parallel to the symmetry plane of the monoclinic crystal, and the normal to the plate is the β axis of the indicatrix. When the crystal plate is at the 45° position or thereabouts the vibrations, occurring in the vertical plane, of the light received by the plate from the polariser, all of which are in the same phase, are resolved by the crystal into vibrations occurring in its own two planes of vibration, and these two rays are again similarly resolved by the analyser into vertical and horizontal vibrations, but each separately. For their velocities are different, and thus the phases are altered with respect to each other. Those two component rays (one of each velocity) which are vibrating parallel to the analyser are then permitted to escape to the observer or the screen, while the other pair vibrating perpendicularly thereto are both extinguished. Hence, two

originally identically similar rays reach the eye or screen; they are of maximum intensity when the plate is exactly at 45°, and are vibrating in the same plane parallel to that of the analyser. But one of them has got behind the other during its passage through the crystal plate, the two, in general, thus differing in phase and being capable of interfering and of producing colour, when white light is used and the retardation of the one behind the other does not exceed seven wave-lengths.

When the analyser is arranged with its plane of vibration parallel to that of the polariser, the crystal plate, whenever its vibration directions (axes of indicatrix) are at the 45° position to the Nicols, shows the complementary colour to that exhibited with crossed Nicols, namely green in the case of a red-green selenite, and yellow with a blue-yellow gypsum film. At the parallel positions of either of the two rectangular vibration directions of the plate with the common plane of the two parallel Nicols, that is, at 0°, 90°, 180°, and 270°, white light uncoloured is seen, the ordinary bright field corresponding to parallel Nicols.

Hence, if the crystal plate be arranged to begin with so that its two rectangular extinction directions (α and γ axes of indicatrix in the case of gypsum) are at 45° to the plane of vibration of the polarising Nicol, and if the analyser be then crossed to the polariser, a colour is produced, red or blue as we have seen in the case of gypsum. On rotating the analyser 90°, that is, until its plane of vibration is parallel with that of the polariser, the complementary colour is afforded, green or yellow when the plate is an adequately thin one of gypsum. Between the two positions, when the analysing Nicol has only been rotated 45°, it being immaterial on which side of zero the rotation occurs, white light uncoloured is transmitted, similar to the ordinary bright field of the parallel Nicols. For, the crystal plate having then a plane of vibration in common with the analyser, that ray thus vibrating passes through the latter unhindered, while the other rectangularly vibrating ray (of the two rays into which the crystal resolves the polarised beam) is simply extinguished, being unable to pass through the analyser. Consequently, in a complete rotation of the analyser, with a film of even selenite arranged with its vibration planes at 45° to the polariser, we observe red or blue twice, namely, at 90° and 270° from the plane of the polariser, green or yellow twice, at 0° and 180° with respect to the polariser, and no colour at the four intermediate positions of 45°, 135°, 225°, and 315° to the polariser.

These somewhat complicated phenomena require to be carefully followed, understood, and remembered, as they are the basis of all the immense assistance which we derive from the polariscopical examination of a crystal. It is obvious that a crystallographic polariscope must be provided with a rotating divided stage for the crystal, as well as with rotating Nicols, each of the latter provided with a divided circle and an indicator or vernier, the one on the mount within which it rotates and the other on the rotating inner tube which actually carries the Nicol.

It will doubtless prove useful to record in concise tabular form the phenomena occurring in the typical case of an "even" film of red-green

selenite. It must be remembered, of course, that the crystal itself is absolutely colourless, the term "red-green" being merely the conventional one to indicate a thin plate of gypsum which affords red under crossed Nicols and green under parallel Nicols.

PHENOMENA AFFORDED IN WHITE PARALLEL LIGHT BY A GYPSUM (SELENITE) FILM, FOR DIFFERENT RELATIVE POSITIONS OF POLARISER, CRYSTAL, AND ANALYSER.

Plane of Vibration of Polariser.	Plane of Vibration of Analyser.	Relations of Nicols.	Positions of Vibration Planes of Gypsum.	Phenomenon observed.
Vertical, | .	Horizontal,—	Crossed, +	45°, ×	Red colour
Vertical, | .	45°, ⟍ or ⟋	⟍ or ⟋	45°, ×	Colourless
Vertical, | .	Vertical, |	Parallel, ‖	45°, ×	Green colour
Vertical, | .	Horizontal,—	Crossed, +	Vertical and horizontal, +	Dark field
Vertical, | .	45°, ⟍ or ⟋	⟍ or ⟋	Vertical and horizontal, +	Half light
Vertical, | .	Vertical, |	Parallel, ‖	Vertical and horizontal, +	Bright colourless field

The red and green referred to in the last column are strictly complementary. For brilliant colours the retardation of one of the two rays should be less than 4λ, and preferably not more then 2λ for very brilliant colours.

The interference of the two components above referred to under crossed Nicols causes total extinction if monochromatic light be used, and if the section-plate of the crystal be of such thickness that one of the two rays on leaving the plate is a whole wave-length before or behind the other. For the additional half wave-length introduced by the analyser then makes the total effective retardation $3\lambda/2$, and the effect of this is practically the same as $\lambda/2$. A total retardation of $5\lambda/2$, due to two whole wave-lengths' difference on leaving the crystal together with the analyser's $\lambda/2$, and also successive retardations of $(2n+1)\lambda/2$, that is, an odd number of half wave-lengths, also cause extinction. Generally, therefore, the section-plate appears dark—when placed with its vibration directions at 45° to those of the crossed Nicols and monochromatic light is used—whenever its thickness is such that the two rays rectangularly vibrating within the crystal and starting therein together in the same phase, differ on emergence by a whole number of wave-lengths, the extra change of phase of $\lambda/2$ due to the analysing Nicol causing this to correspond to darkness instead of the bright field. The monochromatic colour will be transmitted by plates of the intermediate thicknesses, and most brightly when the thickness is halfway, corresponding to an even total number of half wave-lengths of retardation.

That the colours thus afforded by gypsum or any other doubly

refracting crystal, when its vibration directions are at 45° to the crossed and parallel Nicols respectively, are truly complementary, is readily proved by means of a double-image prism, of either the Rochon or Wollaston type described in Chapter XL. (p. 856), employed as analyser instead of a Nicol, and projecting the phenomena on the screen.

The experiment has already been fully described in Chapter XL. and illustrated in Fig. 636 (p. 858). Supposing a red-green selenite to be employed, two images of the circular aperture in front of the lantern, a red disc and a green one, are seen on the screen, more or less overlapping each other, and this lenticularly shaped superposed portion is quite colourless. Such a size of aperture should be selected from the four apertures of the rotating diaphragm shown in Fig. 636 as will give, with the particular double-image prism employed (whether of the Rochon or Wollaston type), an overlapping of the two images of about a third of each disc. If a blue-yellow even selenite be interchanged for the red-green one, the overlapping part will again be quite white.

As the Nicol, the selenite, and the double-image prism are all independently rotatable, the relative positions can readily be found for which the brightest red and green or blue and yellow discs are simultaneously afforded, when the overlapping lenticular-shaped part will be absolutely white, in accordance with the fact that truly complementary colours produce white light.

The explanation of the phenomena observed when the crystal plate is placed with its two possible vibration planes, parallel to the axes of the optical indicatrix, at 45° to the 0° and 90° planes of the crossed or parallel Nicols is as follows. The light from the polariser, vibrating in one plane, is resolved — along these two (mutually rectangular) 45° directions of the axes of the optical ellipsoid, which have been shown in Chapter XLI. (p. 875) to be the only possible directions of vibration within the crystal —into two rays which, after traversing the crystal with different velocities, emerge one retarded behind the other by an amount which depends on the double refraction, the thickness of the plate, and any difference in the length of the path traversed in the plate owing to difference of refraction. They do not yet interfere, however, for they are vibrating in perpendicular planes. The analyser sifts them, however, and again resolves each of these 45° sets of vibrations into 0° and 90° vibrations, and then permits to pass only that component of each which is vibrating parallel to its own vibration direction. The pair of components thus allowed to pass, as they are vibrating in the same plane, are pre-eminently in a condition to interfere in accordance with their difference of phase and, as regards quality of the light, with the total number of wave-lengths by which they are retarded, that is, in accordance with the order of Newton to which they correspond. Also, the analyser resolves the pair in opposite directions, introducing thereby the half wave-length change of phase already referred to as due to the action of the analyser.

Two facts cannot be too emphatically stated. The first is that **for interference to occur the vibrations must be in the same plane**; if they are not, in general elliptic vibrations result from the combination of two rays polarised in different planes, and in the special case when the planes are at right angles, the amplitudes equal, and the phase difference a quarter of a wave, vibrations in a circular orbit are produced. The second fact is that **it is the function of the analyser to reduce the two perpendicular sets of vibrations derived from the crystal to the same plane**, and thus render them capable of interfering.

When white light is used, the colour which is observed is the product of the residual vibrations of different wave-lengths left after the vibrations of a particular wave-length have been extinguished, the complementary colour to the one having that wave-length naturally prevailing. Hence also is explained the complementary nature of the colours afforded when the analyser is respectively crossed and parallel to the polariser, as will be more precisely shown from experimental data later in this

chapter (p. 906). **For the intensity in any angular position θ of the analyser is complementary to that in the perpendicular position θ + 90°**, the sum of the two intensities being equal to that of the incident light after deducting any loss due to absorption and reflection. Hence the rotation of the analyser by 90° changes either the intensity or the tint into the complementary.

The intensity of the colour depends, as we have seen, on the number of the order of Newton to which the total retardation corresponds, which in turn depends both on the thickness of the plate and the amount of the double refraction. The colours of the second order are most brilliant, hence the advantage of a retardation of about two wave-lengths only.

Both monoclinic gypsum (selenite, hydrated calcium sulphate, $CaSO_4 . 2H_2O$) and trigonal quartz (silica, SiO_2) are brilliantly polarising mineral crystals, the former in the thin cleavage films which have already been so much referred to, and the latter both in thin plates such as those of ordinary rock sections (which are usually of 0·04 millimetre thickness or thereabouts) as well as in thicker section-plates up to seven millimetres thick; for although the double refraction is about the same for both minerals, $Na_{\gamma-\alpha}=0{\cdot}0092$ for selenite and $Na_{\epsilon-\omega}=0{\cdot}0091$ for quartz (positive uniaxial), the latter in addition possesses the property of rotation of the plane of polarisation, which introduces further brilliant colour phenomena when the thickness increases up to the limit of seven or eight millimetres (and feebler colour for much greater thicknesses), and the plate is cut perpendicularly, or nearly so, to the optic axis. The fact of the brilliant polarisation of quartz in thin films, however, due to the double refraction, is of great importance in petrology, for it is characteristic of the mineral to show in such sections first and second order colours, and without twinning in the vast majority of cases; hence quartz is the most easily recognised of all mineral crystals under the polarising microscope. The latter is essentially a microscope carrying also a polarising and an analysing Nicol prism, the former below and the latter above the object stage; Chapters LII. and LIII. will be devoted to its construction and use. Crystals having feebler double refraction than gypsum show brilliant colours in thicker plates, a greater distance requiring to be traversed to effect the same retardation. On the other hand, crystals of much higher double refraction than selenite, such as calcite (negative uniaxial), one of the most highly doubly refractive of substances, for which $Na_{\omega-\epsilon}=0{\cdot}1719$, only show brilliant colours in films excessively thin, ordinary thin plates exhibiting white of the higher orders, or only very feeble and impure colours containing much white light.

When the section-plate is thicker than corresponds to a retardation of 7λ, white light of the higher orders is observed instead of colour. When rotated between crossed Nicols, therefore, such a doubly refracting crystal plate merely becomes four times dark (at the positions where its two rectangular vibration directions coincide with those of the Nicols) and four times light (at the 45°-diagonal positions); this is the ordinary case observed in determining extinction angles already referred to on page 898.

The conditions in the very frequently occurring and typical case of gypsum (selenite) will be rendered clear by Fig. 662, which shows the shape of the section-plate (cleavage film) parallel to the symmetry plane $b = \{010\}$ of the monoclinic crystal, the crystallographic axes a (inclined) and c (vertical), and those of the optical indicatrix (γ the first median line and α the second median line). There are also indicated on the figure the positions of the poles of the three pairs of principal faces of the orthozone perpendicular to the section, which bound the latter, namely, the ortho-pinakoid $a = \{100\}$, the basal pinakoid $c = \{001\}$, and the primary orthoprism $d = \{101\}$. An actual crystal of gypsum has already been represented in Fig. 400 (p. 503).

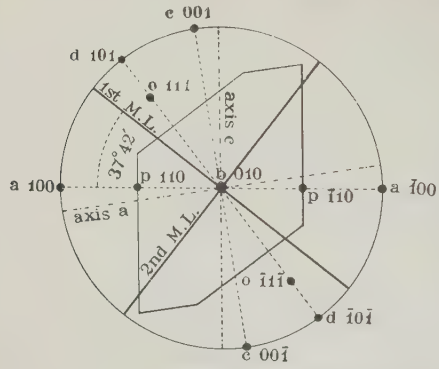


FIG. 662.—Optical Characters of Gypsum Cleavage Film.

The dotted vertical and horizontal lines may be taken as representing the planes respectively of the polarising and analysing Nicols. The vibration planes, extinction directions, of the crystal are represented by the strong continuous lines, the first and second median lines. The light leaves the polariser and enters the crystal vibrating, let us say, parallel to the vertical dotted line. A vibration direction (first or second median line, the γ or α axis of the indicatrix) of the crystal not being coincident with this, but, say, at 45° thereto, the plate having been rotated to bring the median lines so with respect to the vibration direction of the polariser, the rays divide in the substance of the crystal, into two rays vibrating parallel to the first and second median lines respectively: for rays along each of these directions are the resultants of two components vibrating vertically and horizontally. The horizontal component in each case is parallel to the analyser, when the latter is crossed to the vertical polariser, so on reaching the analyser the two rays vibrating parallel to the two median lines are resolved back again into their vertical and horizontal components, and the latter component is in each case transmitted by the analyser. Hence, the crystal plate, if adequately thin for the difference of path between these two transmitted horizontal component rays to be only two or three wave-lengths, appears brightly coloured owing to the interference of the two rays; it appears less brightly coloured when thicker than corresponds to 3λ but not so much as affords 7λ difference, while if thicker than corresponds to 7λ it appears brightly illuminated with white light, on the dark field of the crossed Nicols in each case, the maximum colour or white light illumination appearing when the median line directions are at exactly 45° to those of the Nicols. The thickness of plate required to give the same colour will be the same for all such cleavage plates of gypsum, all being parallel to the symmetry plane of the monoclinic crystal.

In general, the thickness of a crystal plate required to give the same colour will be the same for all sections of the same substance cut in the same direction. But it will be obviously different for differently orientated section-plates, as the difference of refraction, and therefore of velocity, of the two rectangularly vibrating rays will vary.

Practical Use of a Sensitive Gypsum Plate. — A very thin even selenite film which gives in the dark field of the polariscope the red of the first order [1] is particularly useful for determining the character of the double refraction and orientation of specific axes of the indicatrix of a microscopic or other thin crystal; that is, it enables us to distinguish which of the two directions of extinction in a doubly refracting crystal plate corresponds to the lower, and which to the higher, refractive index. For when the field of the polariscope, using crossed Nicols, is filled with the red tint, if such a crystal be introduced in addition, say on the stage of the polariscope or polarising microscope, the selenite being inserted in a slot in the optical tube provided for the purpose, the colour must be altered within the limits of the crystal boundary. By the nature of the new colour thus produced in this part of the field we can ascertain whether the crystal is adding to or subtracting from the action of the gypsum. When the red is depraved to the faint yellow or grey of the first order it must be obvious that the crystals are acting in opposite senses, while if the red be enhanced to the blue or bright yellow of the second order the crystal section must be adding its effect to that of the gypsum. Indeed, the crystal may even be so very feebly doubly refractive as to give when alone in the dark field only the grey or other early tints of the first order even in thick plates, yet it will produce a marked effect on the red selenite field.

The directions of the two axes α and γ of the optical indicatrix of the gypsum are, of course, known and marked on its margin, and the extinction directions of the crystal will have been determined. A rise in order of tint on introducing the crystal so that its axes and those of the gypsum are parallel consequently means that the crystal is arranged with respect to the gypsum so that corresponding axes, greater or smaller, are in coincidence, producing superposition effects; whereas a fall in tint indicates that the smaller axis or direction of smaller refractive index of the one is parallel to the greater axis or index direction of the other.

Relations of Double Refraction and Thickness of Plate to Retardation. —The relations between the difference of path d, the thickness of the crystal plate t, and the double refraction at any point corresponding to which the two refractive indices concerned are μ_1 and μ_2, are derived as follows. The number of vibrations occurring in the thickness t for the ray with the wave-length λ_1 is t/λ_1, and for the ray with wave-length λ_2

[1] According to A. Wenzel (*Phys. Zeitschr.*, 1917, *18*, 472) the plate thickness of gypsum giving the best red sensitive tint is about 56μ ($=0{\cdot}056$ mm.). For quartz cut parallel to the axis the best colour is that between the D and E lines of the spectrum, and for quartz perpendicular to the axis the most sensitive is blue-violet.

it is t/λ_2; the difference in the number of vibrations is thus $t/\lambda_1 - t/\lambda_2$, and the difference of path d, referred to the wave-length in air λ_0, is :

$$d = \left(\frac{t}{\lambda_1} - \frac{t}{\lambda_2}\right)\lambda_0.$$

Now the refractive indices μ_1 and μ_2 of the two rays in relation to air are :

$$\mu_1 = \frac{\lambda_0}{\lambda_1}, \text{ and } \mu_2 = \frac{\lambda_0}{\lambda_2}.$$

Substituting μ_1 and μ_2 for these values we have :

$$d = t\,(\mu_1 - \mu_2).$$

That is, the difference of path is equal to the thickness of the plate multiplied by the difference of the two refractive indices (the effective double refraction) at the point in question.

Relation between Thickness of Crystal Plate and Order of Interference Colour.—The wave-lengths of the visible spectrum (see table, p. 798, Chapter XXXVI.), lie between 0·0007950 millimetre, the wave-length of the dark red rubidium line δ in the extreme red, and 0·0003934 millimetre, that of the solar violet calcium line K. When a doubly refracting crystal plate is so thin that the difference of path between its two rectangularly vibrating rays is less than 0·000100 mm. no colour is produced in the polariscope, but the grey of the first order, which becomes deeper and deeper as the plate becomes thinner, until just before the extremity of possible thinness is reached it is black. With a path-difference of 0·000100 mm., $\frac{1}{8}$th of a red wave or $\frac{1}{4}$th of a violet one, a feeble lavender tint makes its appearance. From this to a thickness affording a path-difference of 0·000200 mm. a pale violet white or bright grey prevails, then a bluish, and subsequently a greenish, white appears, until at 0·000300 mm. path-difference we have a bright yellow, that of the first order; at 0·000400 mm. the bright orange of the first order appears, and for 0·000500 mm. a bright red, the red of the first order, which order terminates conventionally just below a thickness corresponding to a path-difference of 0·000600 mm. The most brilliant part is the red of the first order, the maximum brilliance corresponding to a path-difference of 0·000530 mm. Now this is the wave-length of the bright green of the ordinary spectrum, and the red is here displayed predominating at a maximum in the case of a crystal film because the complementary bright green of the wave-length just mentioned is extinguished between crossed Nicols (the vibration planes of the crystal being at 45° to the Nicols) by the interference of the two rays having such a difference of path. When the Nicols are parallel this bright green itself is actually observed, composed of vibrations near 0·000530 mm. wave-length, which are transmitted while the red is extinguished.

The violet which is produced at the conventional end of the first order, about 0·000600 mm., is known as the "sensitive violet," or "transition tint," inasmuch as it passes with a very slight change of

difference of path on one side (first order) or on the other side (beginning of second order) into red or blue respectively. The first order spectrum thus consists in their respective sequence of grey, lavender grey, bluish grey, greenish white, yellowish white, yellow of the first order, orange of the first order, red of the first order, and transition violet.

The blue of the second order is most brilliant for a difference of path of 0·000660 mm., the bright green of the second order for 0·000800 mm. difference, yellow and orange of the second order respectively for 0·000850 and 0·000900 mm., and finally the brilliant red (most brilliant part of the whole series of spectra) of the second order for a difference of path of 0·001060 mm.; this is double that (0·000530 mm.) for the first order red and about 2λ for the bright spectrum green near E of the solar spectrum, which is consequently extinguished under crossed Nicols, leaving the complementary red to predominate. We have next a transition violet of the second order for a difference of 0·001130 mm., and then the beginning of the blue of the third order, for a thickness of plate corresponding to a difference of path of 0·001200 mm., and so on through the third and subsequent orders, until eventually we reach first the white of the higher orders and finally pure white light.

Fox's Wedge.—One of the most useful objects to possess, in order to familiarise oneself with the more important earlier orders of Newton, is an artificial stepped wedge of mica, made up of twenty-four superposed films of this very readily cleaved mineral, the wonderful cleavage of which was discussed in Chapter XXIX. The films are cemented, by Canada balsam in benzene or turpentine, one after another on the top of each other on a circular glass plate of the regulation size, $1\frac{7}{8}$ inch diameter, for projection polariscopical objects; they are so arranged, step-wise, that each does not quite cover the one previously laid down, being one-sixteenth of an inch shorter, leaving a parallel-edged strip of that amount uncovered as shown in Fig. 663. The films are all such as afford one-eighth of a wave retardation for sodium light, indeed they are cut from the same $\frac{1}{8}$th-wave film, that is, one of the two rays transmitted by this doubly refracting crystal film is retarded behind the other to the extent of one-eighth of a wavelength. The mode of selecting such a $\frac{1}{8}$th-wave film, and the theory of its behaviour in polarised light, will be discussed later (page 923) in the chapter. Such a wedge was first constructed by C. J. Fox, and hence bears his name. When placed in the dark field of the polariscope, between crossed Nicols, it exhibits the first three orders of Newton's rings in eight graduated strips for each order. The films are cut out of the large $\frac{1}{8}$th-wave sheet so that the angle of the strips is 45° to the β and γ axes of the optical indicatrix. The second band gives a quarter-wave difference of phase,

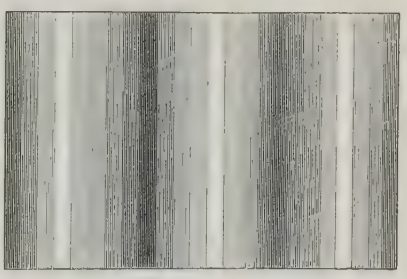


FIG. 663.—Fox's Wedge in Polarised Light between Crossed Nicols.

and the fourth band a half-wave difference, hence an accurately constructed wedge of this kind is a valuable help in constructing quarter or half-wave mica plates, which we shall see later are of great use in crystallographic optics.

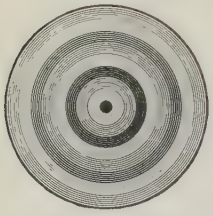


FIG. 664.—Mica Circles of Graduated Thickness in Polarised Light.

Instead of arranging the mica so that parallel narrow rectilinear strips possess successively greater and greater thickness, the layers may be arranged concentrically, so that the strips have a circular annular form, increasing in thickness as the centre is receded from, as shown (with more rapid gradations) in Fig. 664. A reproduction of the effect exhibited in Newton's rings, by crystallographic double refraction, but with the colours in definite narrow annuli instead of graduating more imperceptibly one into the other, is thus afforded. If the slide be put somewhat out of focus the resemblance to Newton's rings is remarkably close.

Concave Gypsum or Quartz Plates.—The crystallographic reproduction of Newton's rings may, however, be effected with the natural gradation very readily and conveniently for projection purposes, by grinding one side of a parallel plate of a doubly refractive crystal slightly concave, the concavity being of spherical curvature of large radius (the larger the greater the double refraction) like the lens in the ordinary Newton's rings experiment. A film of gypsum (selenite) or a plate of quartz serve the purpose best. Fig. 665 is a photographic reproduction of the rings produced, with the projection polariscope shown in Fig. 633 (p. 853), by such a concave selenite film placed on the object stage, the film being cut circular concentrically to the centre of the depression, about an inch and a quarter in diameter, and mounted with balsam between two circular glass plates of the standard size ($1\frac{7}{8}$ inch diameter) to fit the usual mahogany carrier-frames. The Nicols being crossed and their vibration-directions at 45° to those of the concave crystal plate, the effect on the screen is very beautiful and might well be mistaken for a projection of Newton's rings in the ordinary manner, except that the intensity of the colours is probably greater than is commonly obtained on the screen with the latter. Similar spectrum rings are observed when the Nicols are parallel, but they occupy the positions of the white annular interspaces of the ring-system produced when they are crossed. When the analyser is rotated 45° the rings disappear, the field being merely bright with white light, in accordance with the table of phenomena with selenite given on page 901. When a quarter-wave mica plate, to be described in the next

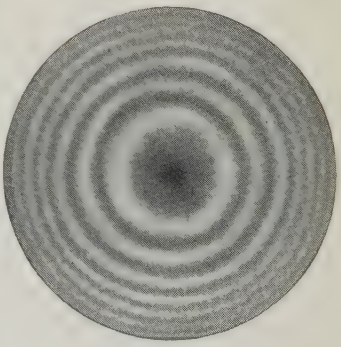


FIG. 665.—Concave Gypsum in Parallel Polarised Light.

section, is also placed with it on the stage facing the analyser, and the latter is rotated, the rings move out from, or inwards towards, the centre, according to the direction of rotation. The quarter-wave plate used should be one with its marked direction γ joining its optic axes parallel to the length of the plate or slide, and not at 45° thereto, assuming the Nicols to have their vibration directions horizontal and vertical, and the quarter-wave plate or slide to be arranged horizontally (right and left) on the stage of the polariscope as usual. The rings of the concave selenite then never extinguish at all as the analyser is rotated, but simply move inwards or outwards to and from the centre.

Quarter-wave and Half-wave Plates.—If a pendulum be suspended from a rectangular pair of gymbals, g and g' being their axes, so as to be quite free to swing in any plane, as in Fig. 666, the path of its bob, if swinging on one gymbal g only, will be ab; but if the swinging occur only on the other g', the path will be cd. Imagining these to be two planes of polarisation at right angles to each other, and the bob a vibrating ether particle, it is easy to see that if, on arriving at the position b at the end of a vibration along ab, when it is at rest just before starting on its return journey to complete the vibration, it receive an impulse from another source to move parallel to cd, that is, along ef, the composition of the two forces will drive it into a circular orbit bod. Such an impulse parallel to the plane cd is given by a wave movement which is one-quarter of a wave behind that along ab. For the latter has moved a half-wave from a to b, and is just ready to start back with adequate force to propel it to a again, the whole wave comprising also this return to a; while the former must have travelled along a half-wave from d to c and then have reached half-way along its way back to d, that is, it must have completed three quarters of its whole double swing, in order to affect the particle b and be in the position to impel it to f. It is clear, then, that at b the second impulse must be a quarter of a wave behind the first impulse in order to propel the particle into the circular orbit.

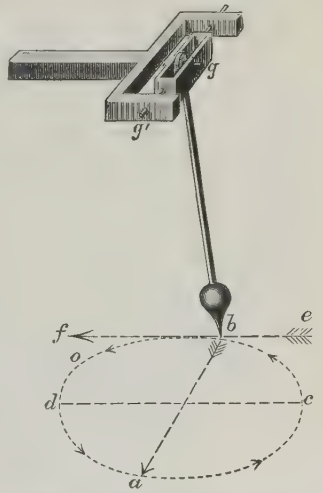


FIG. 666.—Pendulum Experiment illustrating Production of Circular Orbit.

This simple mechanical experiment with a pendulum illustrates the composition of two rectilinear vibrations into a circular vibration by the use of a quarter-wave plate. Equal rectangular vibrations in the same phase compound into one plane vibration inclined at 45° to the original planes. When the phase differs by half a wave the vibrations of the resulting single plane-polarised ray are also at 45° to the original planes, but this diagonal plane is 90° removed from the 45°-plane just referred to, which causes the complementary colours to be shown to those afforded

by the latter resultant. But if the equal rectangular vibrations differ in phase by a quarter of a wave, we now see that a circular orbit results. Intermediate differences of phase afford elliptic orbits.

A half-wave plate consequently reverses all polarisation effects. It makes the bright field dark, or the dark field to become illuminated, and on its addition into the system changes any colour produced with a polarising object into the complementary colour. A very beautiful effect is afforded with a slide of salicine crystals, when a half-wave plate is introduced so as to occupy only one half of the field. Salicine (or salicin) is a bitter but neutral substance (glucoside) of the composition $C_{13}H_{18}O_7$ and the constitution $C_6H_{11}O_5 . O . C_6H_4 . CH_2OH$. It occurs in the bark of certain willows and poplars (*Salix helix* and *amygdalina*, and *Populus tremula* and *græca*). It crystallises in rhombic tablets, but the crystals are usually deposited from solution in one part alcohol and four parts water in radiating circular groups, like wheels, and when placed between crossed Nicols a black cross is produced in each cluster, very much as shown in Figs. 805 and 806, and the cross rotates when the analysing Nicol is rotated. On also now introducing the half-wave mica plate quite close to the salicine slide, the cross rotates in the opposite direction, and if only one-half of the field be covered with the mica the remarkable spectacle is afforded of the black crosses in one semicircle of the field rotating in one direction, and those in the other semicircle gyrating in the opposite direction. This beautiful experiment was shown at the Bournemouth meeting of the British Association in 1919 by the Rev. J. R. Rendel, the slide used having the half-wave mica plate actually mounted on the slide itself, one-half of which it covered, between the crystals and the cover glass. Mr. Rendel has also most kindly prepared for the author a duplicate slide, large enough to cover the whole field of the projection polariscope, $1\frac{7}{8}$ inch diameter, and which affords a magnificent screen picture, the gorgeous colouring of the polarisation between the jet-black arms of the oppositely rotating crosses rendering the whole effect exceptionally

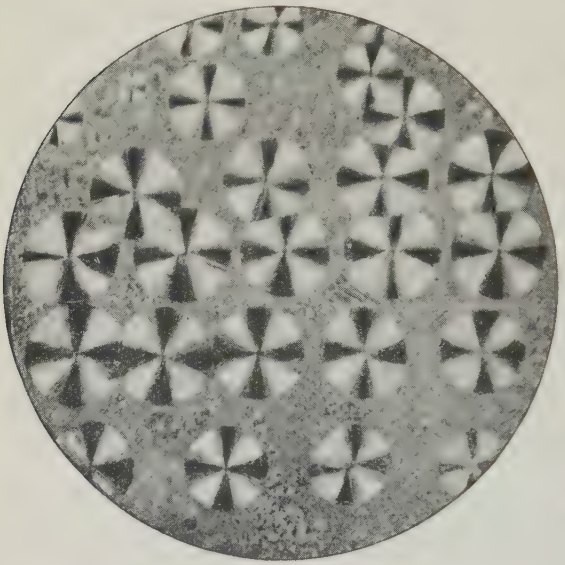


FIG. 666*a*.—Salicine in Polarised Light, between Crossed Nicols.

beautiful. A photograph of the screen picture is reproduced (as far as it is possible to do so in black and white) in Fig. 666*a*.

A quarter-wave plate inserted at 45° to the crossed Nicols, instead of giving colour as a thicker plate would do, gives a bright field with a feeble tint, and the bright field remains so when either of the Nicols is rotated, the tint merely changing from slightly yellowish grey to faintly bluish grey, for positions of the Nicols 90° apart. If sodium light be used the field remains equally illuminated throughout the revolution of the Nicol.

When the experiment is a projection one, and the issuing light is passed through a double-image Wollaston or Rochon calcite prism, a circular aperture in front of the lantern condenser being used as the object projected, as already described in Chapter XL. and illustrated in Fig. 636 (p. 858), the two images of this aperture thrown on the screen will always be equally brilliant. That the light is, however, polarised is proved by inserting an additional polarising object, when such colour as it shows on the screen when the quarter undulation plate is temporarily withdrawn will be changed by a quarter of the Newtonian order which it is exhibiting, when the quarter-wave plate is again inserted in position.

The most convenient substances of which a quarter undulation plate may be made are gypsum (selenite) and mica, on account of the ease with which they cleave into thin plates. Muscovite mica answers the purpose best of all, for this mineral may very readily be cleaved into plates thinner than sheets of paper, and approximately perpendicular to the acute bisectrix of the optic axial angle.

It has been shown in Chapter XXIX. that although muscovite mica is monoclinic, the axial angle β is within a few minutes of 90°, and that the acute bisectrix of the optic axial angle is inclined at less than 2° from the normal to the plane of cleavage, the basal pinakoid $c=\{001\}$; this bisectrix is the axis α of the indicatrix, as muscovite mica is negative in double refraction. The interference figure in convergent polarised light consequently appears apparently symmetrical to the centre of the field of the polariscope, as if the mineral were rhombic. This fact assists us greatly in preparing our quarter undulation plate. For if we select a plate sufficiently thin to show the first ring as a complete ellipse-like lemniscate, as shown in Fig. 667, enclosing both the optic axial brushes, the two rays of light travelling through the plate normally to it will be vibrating in planes which are perpendicular to each other, parallel to the β and γ axes of the indicatrix, and in phases differing by one-quarter of a wave, for light of the middle part of the spectrum, such as sodium light. This will be fully explained a few pages further (pages 913 and 923).

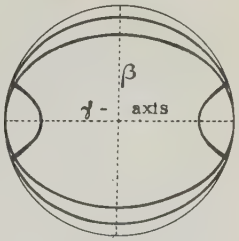


FIG. 667.—Interference Figure in Convergent Polarised Light given by a Quarter-wave Mica Film.

A good even film, as thin as is available, should be selected from the sheets sold in "books" by the mica dealers; this should then be split further by the careful

insinuation of a needle point. After a dozen or more films have been so procured, they should be placed one by one between a couple of glass plates to keep them flat, and examined in parallel light in the polariscope. The particular film required, when inserted with the axes of the indicatrix at 45° to the planes of the crossed Nicols, instead of exhibiting colours when the analyser is rotated, like thicker plates do, will remain unaffected if sodium light be used, and almost so when white light is employed, merely changing as already stated from a faint bluish shade in one part of the revolution, to a pale fawn colour in the other, owing to the quarter-wave relationship not being so perfect for the two ends of the spectrum as it is for Na-light. And when the convergent system of lenses is added to the polariscope it will afford, under crossed Nicols, the figure with one complete ellipse-like ring surrounding both optic axes which is shown in Fig. 667, when the plate is at 45° to the Nicols; when parallel to the crossed Nicols the brushes will join up to form the usual biaxial rectangular cross, the single ring remaining unchanged, and indicating the quarter-wave retardation.

Moreover when a Norremberg "doubler" is available as described in Chapter XLV. and shown in Figs. 732 and 733, and the film is laid on the silvered mirror at the base of the apparatus in the right azimuth, the quarter-wave retardation is doubled to a half-wave; the Nicol analyser adds another half-wave as already explained, and thus the total effect of a whole wave retardation is obtained, so that the light ought to be fully transmitted with the Nicol crossed to the polariser-plate.

When the Nicol is arranged parallel to the polarising plate, the violet transition tint should be given, thus affording an effective test for a quarter-wave film.

The light leaving the quarter-wave crystal film is thus circularly polarised, so that the resolution once more into two plane vibrations by the analyser may occur equally well at any part of the circular orbit; one of these resolved rays is then alone transmitted by the analyser, that parallel to its own vibration plane, while the other will obviously be extinguished. Absolute equality of light as the analyser is rotated is only possible, even with a very accurately chosen quarter undulation plate, for the one monochromatic wave-length used in making the selection, usually sodium light, other wave-lengths on each side being slightly admitted, giving rise to the slight fawn and bluish tints observed in white light, at complementary positions 90° apart during the rotation.

The quarter-wave mica plate should be marked to indicate the direction of that axis (γ) of the indicatrix which joins the positions of the two optic axes. One of its chief uses is to determine the sign of the double refraction of a crystalline substance, before the prolonged operations of the determination of the refractive indices are undertaken; for a characteristically different effect on the interference figure given by a positive and by a negative crystal in convergent polarised light is produced by the introduction of a quarter-wave plate between the crystal plate and the analyser, as will be fully described in Chapter XLVIII. If the quarter-wave plate, therefore, be required for this purpose, for use with the observing polariscope or polarising microscope, it is cut into an elongated oblong shape, with the long sides parallel to the line joining the optic axes, and is mounted with balsam between two similarly shaped truly plane and parallel-surfaced glass strips, about 6 centimetres long and 11-12 millimetres wide. The shape of the plate is thus an adequate indication of the direction of the γ axis of the indicatrix passing through the optic axes.

If the quarter-wave plate be required for lantern polariscopical projection work a larger film is used, and mounted between two circular glass plates of the usual size, $1\frac{7}{8}$-2 inches diameter, for insertion in the rabbet of a standard mahogany mount 4 by $2\frac{1}{4}$ inches in size, the circular aperture of which, that of the containing rim of the rabbet, has the regulation diameter of $1\frac{5}{8}$ inches. The composite disc of quarter-wave film and glass is held in position in the rabbet of 2 inches diameter by a not quite complete ring of brass wire, the free ends acting as a spring. The disc should be rotated into the position in which the quarter-wave plate is required, before pressing the wire ring home, and it is advisable that the periphery of the disc should be engraved with a dot or other mark at both ends of the diameter joining the positions of the optic axes.

As a matter of convenience it is a great advantage to have two such quarter-wave plates for projection purposes, one mounted with this marked diameter parallel to the length of the frame, and the other with it at 45° thereto, a position in which it is much required. As two quarter-wave plates are frequently simultaneously used in projection experiments, the possession of a second film is, in fact, essential anyhow. The special stage to take both these quarter-wave plates at once if desired, with a third polarising crystal or other object plate between them, all three mounted in their mahogany frames, is shown under the optical bench in Fig. 633 (p. 853).

When the quarter-wave plate is arranged with its vibration directions, the indicatrix axes β and γ (the latter the diameter joining the optic axes just referred to and the former the perpendicular diameter), parallel and perpendicular respectively to the plane of vibration of the polarising Nicol no effect is produced, the plane-polarised beam passing through unaffected. But when a crystal plate with vibration directions at 45° precedes the quarter undulation plate, the vertically or horizontally vibrating beam from the polariser is resolved by the former into two diagonally (45° to the vertical and horizontal) vibrating rays, and the quarter-wave plate arranged vertically and horizontally again resolves these. Thus the use of a quarter-undulation plate is generally only effective when its planes of vibration are at 45° to those or that of the preceding object, whether it be a polarising crystal or the Nicol polariser itself. And as the preceding polarising object will sometimes have its planes of vibration vertical and horizontal and sometimes diagonally arranged at 45°, according to the nature of the experiment, it is very convenient to have two quarter-wave plates always ready, one mounted diagonally and the other parallel to the frame edges, so as to be always prepared for either case.

To determine the direction of revolution of the circularly polarised light afforded by a quarter-wave plate, it is placed between crossed Nicols with its plane truly perpendicular to the axis of the beam of incident light, and in an azimuth such that the restored light is a maximum. The principal directions in the plate now make angles of 45° with the directions of vibration of the Nicols. The plate should then be rotated, first round one principal direction, then around the other, so that the light traverses a thicker layer of mica. In one case the colour passes from bluish-grey

through iron-grey to black; in the other case through white to yellow and interference colours of a higher order. The latter corresponds to rotation about the direction parallel to the slower vibrations, and this direction should be marked "slow"; the first case corresponds to the perpendicular direction of faster vibrations, and should be marked "fast." By reflection at a grating, or any other mirror, the direction of revolution of the polarised light in a quarter-wave plate is reversed.

The Quartz Wedge.—It has been shown in Chapters XXII. and XXXIX. that quartz is a positive uniaxial substance belonging to the trigonal system, having a refractive index for the ordinary ray of $\omega = 1{\cdot}5443$, and for the extraordinary of $\epsilon = 1{\cdot}5534$, the amount of the positive double refraction being thus $\epsilon - \omega = 0{\cdot}0091$. This amount is relatively small, only one-nineteenth of that of negative calcite (for which $\omega - \epsilon = 0{\cdot}1719$). The ordinary ray may travel in quartz, as in all uniaxial crystals, not only along the singular axis, the unique optic axis, but in any direction through the crystal equally, the wave-surface being a sphere. But it always vibrates in the circular section perpendicular to the axis, so that ω corresponds to all vibrations perpendicular to the axis, and ϵ to vibrations parallel to the axis, but only when the direction of propagation is perpendicular thereto in the circular section.

When a section-plate is cut, ground, and polished from a prismatic quartz crystal along the direction of the prism, parallel to the optic axis, vibrations in the direction of its length will correspond to ϵ, the greatest refractive index as in the case of the mica quarter undulation plate, while those perpendicular to the length and therefore to the axis will correspond to the minimum index ω. When the section is made to taper slightly, that is, wedge-shaped, as represented in elevation at *a* in Fig. 668—the two faces being true planes meeting in an edge which is perpendicular to the length of the wedge, and inclined at a very small angle to each other, and prepared so carefully that the greatest possible tenuity shall be attained at the thin end—such a wedge of quartz will exhibit in the dark field of the polariscope arranged for parallel light, and best when the wedge-length is arranged at 45° to the crossed Nicols, several of the orders of spectra of Newton's scale, starting from the thin end, as shown diagrammatically at *b* in Fig. 668. The wedge may, in fact, be imagined to be a strip, radiating from the centre, cut out of the concave quartz disc (a plate one side of which has been ground concave) referred to on page 908, except that both surfaces are now true planes slightly inclined; or it may equally well be considered as a strip cut out of the Newton's ring apparatus itself, except that the tapering film is here quartz instead of air, and that the second surface is a true plane instead of being a curved surface of large radius. Also the interference is due to the difference of velocity of the two rays produced by double refraction, instead of being due to reflection from the two surfaces of the wedge. The effect of the regularly increasing thickness is to increase the retardation of one ray, the slower extraordinary ϵ ray vibrating parallel to the length of the wedge, behind the other, the ordinary ray ω vibrating parallel to the edge of the wedge.

The wedge requires to be very carefully cut to show the first black band, owing to the brittleness of quartz and the consequent difficulty of attaining great tenuity with the mineral. Only one, cut by Messrs. Steeg & Reuter, out of several in the possession of the author, exhibits the band to perfection. Usually the wedge begins at the thin end by showing the faint grey and then the yellow of the first order spectrum. The junction of the first and second orders is a strikingly brilliant band coloured deep red on the thinner side and deep blue on the thicker, with dark violet or purple between. Each successive junction-band of two successive spectra becomes less striking than the one before it; the second appears red on the thinner side and purplish blue on the thicker, without the deep purple centre; the third is rose pink on one side and green on the other, and so on, with accession of more and more white

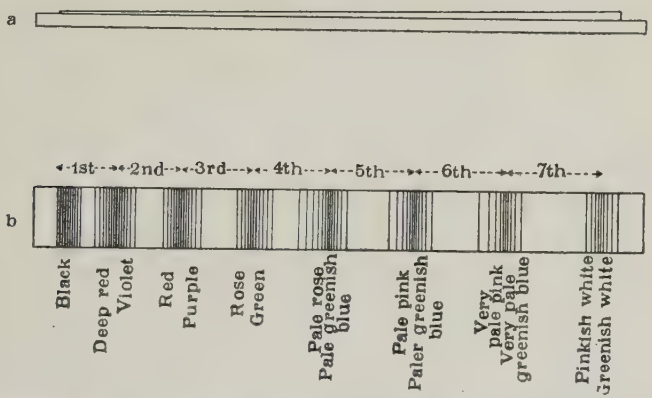


FIG. 668.—The Quartz Wedge, in Section at *a*, and the Seven Orders of Spectra afforded by it in Parallel Polarised Light at *b*.

light, until the end of the seventh order is reached, when the tint is almost pure white. The succession of spectra is diagrammatically represented and the order of colours stated in the lower part *b* of Fig. 668.

Obviously, the smaller the angle of the wedge the more extended are the spectra, and a wedge which only just shows the seven orders in about two inches of length is perhaps the most useful of all, although for some purposes one showing only the first three orders in this length is very convenient. It is advisable to have at least one such quartz wedge of the same elongated dimensions as the quarter-wave mica, namely, 6 centimetres by 11 to 12 millimetres. It is mounted on a glass plate of the same width but a little longer, and in the case of the thinnest showing the black band the quartz is covered with a similar thin glass plate to avoid injury to the fine edge, the mounting being in all cases with Canada balsam.

The use of the quartz wedge in connection with optic axial interference figures will be discussed in Chapter XLVIII.

Crystal Plates in Convergent Polarised Light. — It is a very natural step now from the colour phenomena of crystal plates, wedges, and concave plates in parallel polarised light to those exhibited when the light rays are made to converge. A further factor is now introduced, namely, different obliquity of the rays in the various parts of a conical beam of light. Hollow cones of ever-widening angle, one outside another, succeed each other as the axis of the cone is departed from, corresponding for a specific thickness of plate and for light of a definite wave-length to differences of phase between the two rays travelling along the surface of each cone, with velocities varying differently with the angle of the cone, of whole wave-lengths, that is, to λ, 2λ, 3λ, and so on, of retardation.

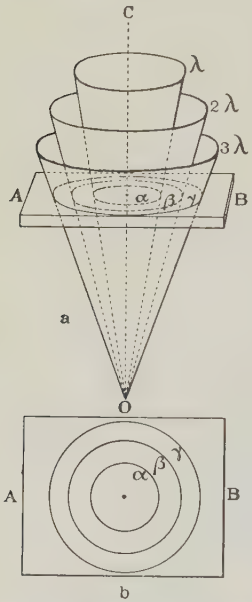


FIG. 669.—Passage of a Conical Beam of Light through a Uniaxial Crystal Plate perpendicular to the Axis.

Let us take the simplest case first, that of a plate of a uniaxial crystal cut perpendicularly to the trigonal, tetragonal or hexagonal axis. We have seen that along this axis there is no double refraction, while in all directions at right angles thereto there is a maximum of double refraction, and that the optical ellipsoid is one of revolution. In the diagram at *a* in Fig. 669 OC represents the optic axis, and the three cones one outside another may be taken to represent conical surfaces along which, for a section-plate AB of some convenient thickness and for monochromatic light of some specific wave-length, the difference of phase between the ordinary and extraordinary rays ω and ϵ—due to progressive difference of velocity between the two rays as the axis of no double refraction is left and the maximum difference for rays travelling in the circular section is approached, and also as the thickness of plate traversed increases with the obliquity—is respectively λ, 2λ, and 3λ. Such a section-plate of the crystal will cut the cones in circular sections α, β, γ, shown in perspective at *a* and in plan at *b* in Fig. 669, these concentric circles becoming closer as the centre is receded from, as in the case of Newton's rings. At the centre, where there is no double refraction, the ordinary and extraordinary rays are composed of vibrations both sets of which are perpendicular to the axis, their direction of propagation, and parallel to the circular section of the optical ellipsoid ; they travel, therefore, with the same velocity, so that the waves will be in the same phase. They correspond to the same refractive index ω, and are thus identically similar, except that their vibrations may occur in any azimuth of the circular section, there being no tendency to vibrate in one principal section (plane containing the axis) rather than another. After traversing the plate along the surface of the cone λ, however, and more still at the cones 2λ, 3λ, and successive ones, a difference has manifested itself, due both to the fact that double refraction

has revealed itself, involving different velocity and refractive index of the two mutually rectangularly vibrating rays into which the light is divided, and that with increasing distance from the centre the rays have longer and longer distances to travel in which such retardation can develop. One ray vibrates still in the circular section and perpendicularly to the principal section containing the axis and to the ray, and affords the index ω; the other vibrates at right angles thereto in the principal section and perpendicularly to the direction of propagation, and with refractive index more and more removed from ω in the direction of ϵ as the centre is receded from. The retardation of the one behind the other (whether ω or ϵ is the slower depending on which is the greater refractive index) is equal to exactly one wave-length λ at any point on the circle of intersection α of the first cone by the exit surface of the plate, to 2λ at any point on the second circle β in Fig. 669, to 3λ on the third circle γ, and so on.

Consequently, when the crystal plate is observed between crossed Nicols in a conical pencil of rays, produced by a strongly converging lens-system, these circles should appear bright and the intervening annuli dark. But we have to remember that the analysing Nicol, as explained on page 898 in connection with the occurrences in parallel light, also introduces a change of phase of half a wave-length, so that the circles corresponding to whole wave-lengths of retardation of one ray behind the other really appear dark in the monochromatic light employed, and the intervening spaces bright. The centre is not only a black spot, as in Newton's rings, but is also the centre of a black rectangular cross radiating through the circular rings, marking the directions of the planes of vibration of the Nicols. For both at the central part where there is no double refraction, and in the cross, the dark field prevails, the rings having their maximum clearness in the 45° diagonal positions.

If the circular rings α, β, γ shown in Fig. 669 were produced in yellow sodium light, those for red light would be wider apart, and those for blue light closer together, the distance varying regularly with the wave-length according to a law similar to that already explained for Newton's rings. If ordinary white light be employed, the circles will represent the colour which is extinguished, and therefore along such circles the complementary residual colour will predominate. Hence the black rings of monochromatic light become circular spectra in white light, just as in the case of Newton's rings

For a biaxial crystal very similar considerations apply. The two optic axes will be, within the limits of error appertaining to the determination of the optic axial angle, lines of no double refraction, but the conical surfaces of λ, 2λ, 3λ, and so on, of retardation will now be of oval section, corresponding to the lower symmetry of rhombic, monoclinic, and triclinic crystals. The double refraction along any line in each case is measured by the difference between the axes of the section of the indicatrix perpendicular to it. Fig. 670 will help to render the case of a biaxial crystal clear. The sections of the two series of cones of equal retardation about the two optic axes, by a plate perpendicular to the

bisectrix of the acute angle between the latter, are indicated in dotted lines.

Before passing to the further consideration of the more complicated

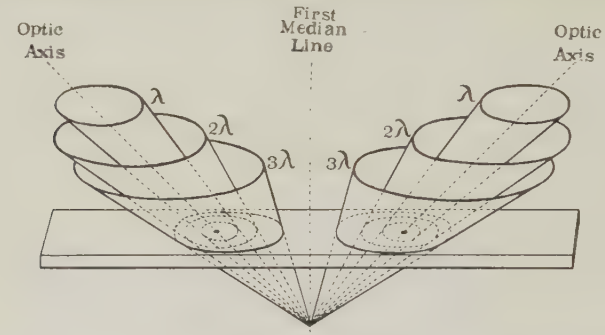


FIG. 670.—Passage of Convergent Polarised Light through a Biaxial Crystal Plate perpendicular to the First Median Line. Cones of Equal Retardation about the Two Optic Axes.

biaxial phenomena, another mode of considering the uniaxial case is instructive.

Suppose *abcd* in Fig. 671 to be a section of a uniaxial plate perpendicular to the optic axis CC′. The section of the plate shown in the figure is a principal section, as it is parallel to the unique optic and singular crystallographic axis. Assuming the Nicols crossed and the particular section *abcd* arranged at 45° to the vibration directions of the Nicols, and that monochromatic light is employed, a central ray in the converging bundle passing along CC′ from C′ to C, will suffer no double refraction, and the field in the centre will consequently appear as if no crystal plate were there, namely, dark. But a ray such as *ef*, inclined to CC′, will be more or less doubly refracted, the plane polarised light from the polarising Nicol being resolved into two rays *fg* and *fh*, an ordinary and an extraordinary ray, vibrating at different rates, one (the extraordinary) in the section *abcd* and the other (the ordinary) in a plane at right angles to the section. At *h*, however, the oppositely vibrating component of an adjacent ray *kl* will also emerge, and as all the rays on emergence follow a direction parallel to the original ray these two rays will proceed from *h* in company, but without interference owing to their planes of vibration being at right angles. The analysing Nicol again resolves each of these and permits the two components, one from each, which are vibrating

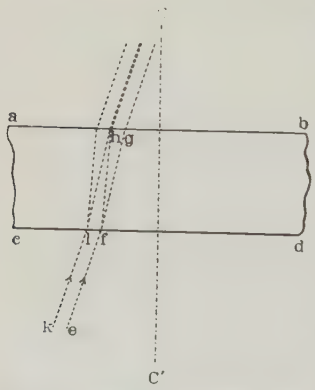


FIG. 671.—Passage of Convergent Polarised Light Rays through a Uniaxial Crystal Plate perpendicular to the Axis.

parallel to its own vibration direction to pass, extinguishing the other two. As the two component rays thus transmitted by the analyser vibrate in the same plane they are in a condition to interfere, which they do in accordance with their relative phases and the total retardation of one behind the other, due to difference both of path and of velocity of vibration. When this amounts to half a wave-length, instead of the extinction which occurs at the centre where the difference is *nil*, light will appear, and the first dark circular ring will be formed at the locus of points where the retardation amounts to a whole wave-length, and so on, light recurring for annuli corresponding to odd half wave-lengths and darkness to whole wave-lengths of retardation, the ordinary phenomena of interference being thus reversed owing to the half wave-length of difference of phase introduced by the action of the analyser.

Similar points around the axis CC′, where components of the ordinary and extraordinary rays interfere to the same extent, must obviously lie on a circle, and such circles for which the difference between the pairs of interfering rays is $\lambda/2$, $3\lambda/2$, $5\lambda/2$, and so on, must appear as bright rings in concentric succession, coloured according to the tint of the monochromatic light used; for the double refraction constantly increases as we recede from the centre and approach the maximum at right angles to the axis. The intervening annuli will be dark, the maxima of darkness occurring for circles of exactly λ, 2λ, 3λ, and so on, as at the centre where the difference is zero.

Hence, a figure of concentric circles of alternating light and darkness is produced, as shown in Fig. 672, where *ab* is the plane of the section *abcd* of Fig. 671, the crystal plate itself being assumed to be parallel to the paper; the central point is that of emergence of the optic axis, and the directions 0°-180°, 90°-270° are those of the vibration planes of the polarising and analysing Nicols respectively.

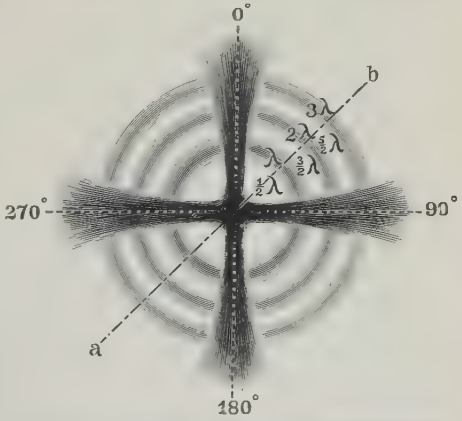


FIG. 672.—Interference Figure of Concentric Circles and Dark Cross afforded by Uniaxial Crystal Plate perpendicular to the Axis in Convergent Polarised Light.

What occurs in the section *ab* 45° to the planes of the Nicols, or the analogous one 45° on the other side at right angles to *ab*, occurs similarly but with less intensity in all other directions, as there is symmetry round the optic axis; hence, we obtain the concentric circular rings of maxima and minima of light. There is a gradual transition from light to darkness, so the figure in monochromatic light is a soft one without sharp circular lines, the central umbra of each dark band being bordered on each side with a penumbra, fading away into the bright ring

adjoining, which also varies in intensity up to a central most brightly illuminated circular line, softly falling off in brilliance on each side.

The black cross, having arms sharp near the centre but spreading out and shading off near the extremities, is produced because the intensity of the light is due to the sum of the two amplitudes of the two component rays which reinforce or interfere, and this is a maximum at the two 45° diagonal positions and a minimum in the 0°-180° and 90°-270° directions, the Nicols being assumed to be crossed as throughout the above discussion of the phenomena.

The distance of the rings from each other for one and the same wave-length diminishes as the centre is receded from. On varying the wave-length the separation of the rings alters; they close up nearer to each other with shortening wave-length, as the blue end of the spectrum is approached, and open out when the wave-length is increased, as the red end is approached.

When white light is employed the extinction of a particular colour at any point, on account of the difference of path of the two rays for that colour amounting to a whole wave-length, leaves the complementary colour predominating, and so spectrum-coloured rings are produced instead of black ones. The cross, however, remains black.

Increase of the thickness of the plate of the same substance causes the rings to close up, less obliquity being required to afford the same relative retardation and length of path of the two rays on passing through the crystal; while diminution of the thickness causes their expansion, a greater obliquity being obviously required to afford the same relative retardation and length of path through the crystal.

Careful reproductions of actual photographs, taken by the author, of the interference figures in convergent polarised yellow light afforded by plates of two uniaxial crystals, those of trigonal calcite and hexagonal apatite, cut perpendicularly to the optic axis, are given in Figs. 673 and 674 on the adjoining Plate IV. The crystal plate was very thin in the case of calcite, and very thick in the case of apatite, the former being a substance of very large double refraction ($\omega - \epsilon = 0{\cdot}1719$ for Na light) and the latter one of small birefringence ($\omega - \epsilon = 0{\cdot}0044$ for Na light). Fig. 674 is also similar to that afforded by a slightly thinner plate of calcite than that used for the production of Fig. 673. The two Nicols were crossed in each case, and their vibration directions were vertical and horizontal respectively when the photograph was taken for Fig. 673, but they were rotated 45° to these directions for Fig. 674. The arms of the dark cross thus follow these vibration directions of the Nicols.

Rotation of the section-plate does not alter the uniaxial figure. This will be clear from the interference figure of apatite in Fig. 674 of the adjoining plate; for the figure was photographed with the crossed Nicols simultaneously rotated to the diagonal positions as just stated, which is equivalent to a rotation of the plate for 45°. The effect is merely to rotate the cross round 45°, its arms following the directions of vibration of the crossed Nicols. The figure itself is identical, and the only difference is as regards the position of the cross with respect to the edges of the page.

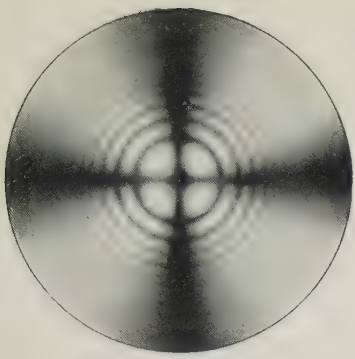


FIG. 673.—Uniaxial Figure given by Thin Plate of Calcite (Trigonal) perpendicular to the Axis. Vibration Planes of Nicols Vertical and Horizontal.

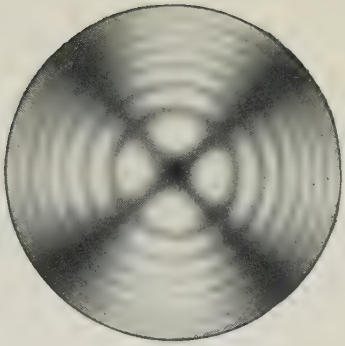


FIG. 674.—Uniaxial Figure given by Thick Plate of Apatite (Hexagonal) perpendicular to the Axis. Vibration Planes of Crossed Nicols arranged at 45°.

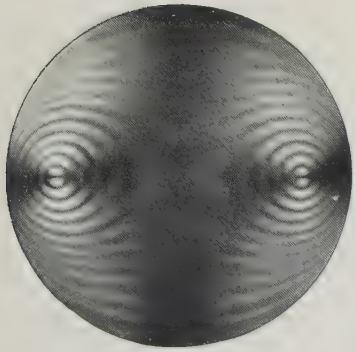


FIG. 676.—Biaxial Figure given by Cleavage Plate of Mica (Monoclinic) perpendicular to the First Median Line. Nicols Vertical and Horizontal.

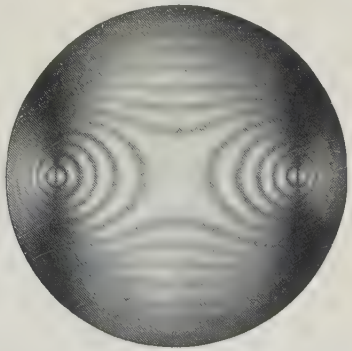


FIG. 677.—Figure given by the same Mica Plate when the Crossed Nicols have been simultaneously rotated 45°.

REPRODUCTIONS OF DIRECT PHOTOGRAPHS OF INTERFERENCE FIGURES AFFORDED BY CRYSTAL PLATES IN CONVERGENT POLARISED YELLOW LIGHT.

Plate to face page 920.

But rotation of the analysing Nicol to parallelism with the polariser causes the complementary phenomena to be produced, namely, in monochromatic light a bright cross, and black rings where under crossed Nicols bright rings had appeared, and in white light a white cross and complementarily coloured rings to those appearing with crossed Nicols. The reproduction of a photograph in white light is given in Fig. 675.

FIG. 675.—Interference Figure afforded by Calcite with Parallel Nicols.

A Plate of a Biaxial Crystal cut perpendicularly to an optic axis affords very similar phenomena, but the rings or curves of equal retardation are not circles, although they often resemble circles very closely, as in the case of gypsum, the figure for which has already been shown in Fig. 611 (p. 833); they are really ellipse-like curves of the kind known in analytical geometry as lemniscates. The black cross is now only represented by a single bar, which, moreover, is only straight when the section-plate is arranged with the plane of the optic axes (one of the three principal planes of the optical indicatrix) parallel to one of the vibration directions of the crossed Nicols; in other positions the bar becomes a hyperbolic curve with expanded tails but sharply outlined vertex, the latter passing through and being pivoted on the site of the optic axis. The ellipse-like rings one outside another are symmetrical to the rectilinear direction of the straight black bar, but in the direction of the bar the pivot position occupied by the hyperbolic vertex, marking the optic axis when the plate is rotated, is nearer to the ring on one side than on the other, the relations being as the differences of the intermediate refractive index β from the two extreme indices; on one side the distance between the pivot position and the ring will be proportional to γ-β, and on the other to β-α.

The first (innermost) dark ring in monochromatic light corresponds to a retardation difference, of one of the two rays which interfere, behind the other, of one wave-length, λ. The second ring corresponds to a difference of two wave-lengths, 2λ, the third to 3λ, and so on. As explained for a uniaxial plate, these whole-wave-length differences correspond to darkness rather than to light on account of the additional half-wave-length change of phase introduced by the action of the analyser.

When the section-plate is cut perpendicularly to the bisectrix of the acute angle between the optic axes both sets of rings appear in the field, one on each side of the centre, the black bar of the two joining up to form a continuous straight line running through both optic axes, when the plane of the latter is arranged parallel to a plane of one of the crossed Nicols; it is crossed at the centre by the rectangularly transverse bar corresponding to that of the cross of the uniaxial figure, but relatively very much broader and less black and sharp than the one joining the optic axes, which is very clearly defined at and between the optic axes and until it gets near the margin of the field.

The figure afforded by a fairly thick cleavage plate of muscovite mica is shown in Fig. 676 (the third figure on Plate IV.), which is the reproduction of a direct photograph by the author. It has already been explained that the cleavage plane of this variety of monoclinic mica is within 2° of being exactly at right angles to the acute bisectrix of the optic axial angle, which latter is sufficiently large, about 75° in air, to show the axial "eyes" very well separated in the field of the polariscope.

When the section-plate is rotated, the black cross of a biaxial figure opens out into two hyperbolic curves or "brushes," like the one just described as being shown, passing through the single optic axis, by a plate cut perpendicularly to one axis only, the vertex of each hyperbola being sharp and pivoted on the position of emergence of the optic axis. This will be rendered clear by Fig. 677 (the fourth figure of Plate IV.), which is a reproduction of another photograph taken when the crossed Nicols had been simultaneously rotated (as is possible with the "Dick" crystallographic microscope constructed by Swift) for 45°, that is, to the diagonal positions. Such simultaneous rotation of the Nicols is obviously equivalent to the rotation of the plate, and is frequently much more convenient.

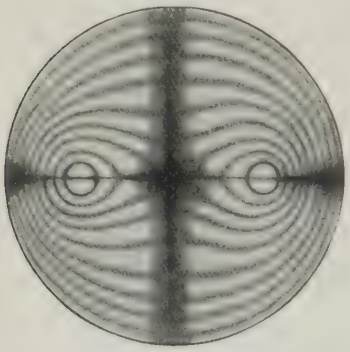


FIG. 678.—Biaxial Figure. Vibration Directions of Plate and Crossed Nicols Parallel.

The effect of actually rotating the plate itself, however, the Nicols remaining fixed in their horizontal and vertical fixed positions, is shown in two stages in Figs. 678, 679, and 680. Fig 678 represents the original

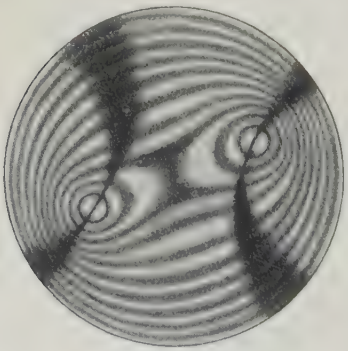


FIG. 679.—Biaxial Figure after Rotation of Plate for 22½°.

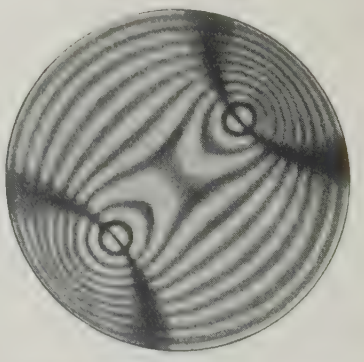


FIG. 680.—Biaxial Figure after Rotation of Plate for 45°.

position, the plane of the optic axes being parallel to the plane of vibration of one of the Nicols. Fig. 679 is the figure afforded when the plate has been rotated 22½°, and Fig. 680 when the rotation amounts to 45°. When

the rotation has attained the midway 45°-position the figure is suitable for the measurement of the optic axial angle, by successive placing of the vertices of the brushes to the cross-wires, by rotation of the plate about a transverse axis perpendicular to the plane of the optic axes. For the vertical spider-line becomes a tangent to the vertex in each case, and if a pair of vertically parallel spider-lines are employed, as shown in Fig. 681, adjustable at a distance apart just greater than the thickness of the brush at the vertex, the latter can be delicately adjusted between them. The two vertices are preliminarily adjusted so as to be bisected by the single horizontal spider-line, and to remain so on rotation of the section plate. A detailed description of the mode of measurement will be given in Chapter XLVIII.

With plates of different thickness the optic "brushes" remain constant, except that the sharpness of their vertices becomes diminished as the plate becomes thinner than that showing several complete rings round each axis, which is the figure of suitable sharpness for the purpose

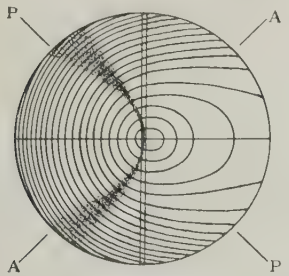


FIG. 681.—Adjustment of Optic Axial "Brush" to Spider-lines.

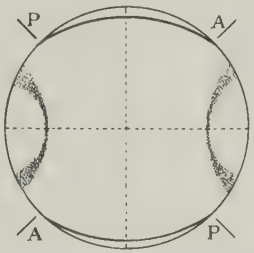


FIG. 682.—Figure given by Mica affording ⅛ Wave Retardation.

of measurement of the optic axial angle. The rings rotate with the plate, maintaining their relative positions. The number of complete rings round each axis depends on the thickness of the plate, as will be clear from what has already been stated; the thicker the plate, the more numerous, smaller, and sharper the rings, as the number of complete wave-lengths of retardation, corresponding to complete rings round each axis, increases with the thickness. Thus, for instance, four plates of muscovite mica of graduated thicknesses afforded the interference figures shown in Figs. 682, 683, 684, and 685. The first (Fig. 682), the thinnest plate, was a film for which the difference of path within the crystal was such as to bring about a retardation of one ray behind the other amounting to one-eighth of a wave; no complete ring is shown, the first lemniscate being of ellipse-like character enveloping both axes, near and partly outside the margin of the field. The figure afforded by a quarter undulation plate of mica has already been given in Fig. 667 (p. 911), and comes next in order, showing one entire lemniscate surrounding both axes and a second curve partially visible outside it. The second figure now shown, Fig. 683, was afforded by a still thicker plate corresponding to half a wave-length of retardation; no complete ring is again visible, but there are six lemniscates

now in the field, the innermost of which is bending in at the centre to form the approach to a loop. The third (Fig. 684) cleavage film is again thicker, and exhibits one whole wave-length of retardation, the loop of the innermost lemniscate being just complete, that is, each optic axis is now surrounded by one complete ring. The fourth (Fig. 685) is the thickest plate, and shows exactly two wave-lengths of retardation of one ray behind the other, two complete rings being present round each axis. The drawings were made for sodium light, so that the wave-lengths referred to are those for light of the average wave-length of the D-lines of the spectrum, 0·0005893 millimetre. They were made for the crossed 45° positions of the planes of the polariser PP and analyser AA.

For the same thickness, the number of rings will obviously depend on the amount of the double refraction, γ-α, the rings becoming smaller, sharper, and more numerous as the double refraction increases. Also, when monochromatic light is used, say that of the spectroscopic illuminator described in Chapter XLIV., and the various colours are employed

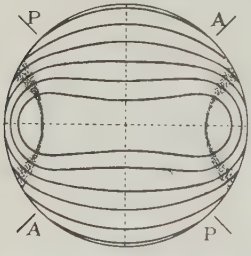


FIG. 683.—Figure given by Mica affording $\frac{1}{2}$ Wave Retardation.

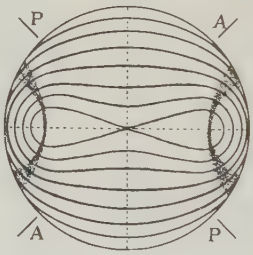


FIG. 684.—Figure given by Mica affording a Retardation of one Wave-length.

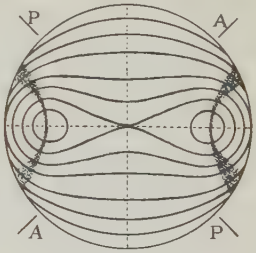


FIG. 685.—Figure given by Mica affording a Retardation of two Wave-lengths.

in succession, the rings will be observed to close up and become more numerous as the red is receded from and the blue end of the spectrum approached, that is, with shortening wave-length.

Outside the last pair of complete rings the next lemniscate is of almost but not quite complete loop form, and the next one or two are still of this character, but the loop is gradually straightening out, after which the lemniscates become more and more ellipse-like and approach nearer and nearer to a circular curvature and become closer together, as the margin of the field is approached.

In white light the figure is similar, but composed, as already stated, of spectrum-coloured rings, loop-lemniscates, and ellipse-like lemniscates, the cross or hyperbolic brushes into which it breaks up on rotation remaining black. It differs essentially, however, from a uniaxial figure, inasmuch as the optic axial angle is different for each wave-length, the succession of colours being almost altogether dominated by this fact, and by the dispersion of the bisectrices, shortly to be referred to. Indeed the phenomenon of dispersion of the optic axes for different wave-lengths goes so far in the cases of " crossed axial-plane dispersion " that the optic axes are situated in one principal plane of the optical ellipsoid for red light, and in a second

perpendicular principal plane for blue light. Hence, the simple succession of colours, as in Newton's rings, observed with uniaxial crystals, is very considerably modified and affected by this essential difference of the conditions. Also, the rings clearly visible in white light cease with the seventh, further spectrum coloured rings being obliterated by white light of the higher orders, whereas in monochromatic light a very large number of rings are visible, only limited in fact by the extent of the field.

It must be remembered that the angle between the optic axes as observed in air, generally denoted by 2E, is larger (on account of the difference of refraction) than the true optic axial angle within the crystal, which is represented as $2V_a$, the suffix a indicating that the symbol refers to the acute angle between the optic axes.

Effect of Symmetry on Biaxial Figure—Phenomena for Rhombic Symmetry.—The biaxial interference figure of a rhombic crystal in either white or monochromatic light is truly symmetrical about its two rectangular diameters, that is, about the central line of the black bar joining the optic axes and the central line of the transverse bar between the axes. For these two rectangular lines are the intersections of the section-plate (itself parallel to one of the principal planes of the optical ellipsoid and to a crystallographic axial plane) with two of the principal planes of the optical ellipsoid, which are identical with two of the crystallographic axial planes. For, the crystallographic axes and those of the ellipsoid being identical in direction, for all wave-lengths of light and at all temperatures, from the very essence of rhombic symmetry, and the acute and obtuse bisectrices or "median lines" of the optic axial angle being identical with two of those axes, there can be no dispersion of the median lines in the case of a rhombic crystal. The only possibility of dispersion is that common to all biaxial crystals, namely, that of the optic axes themselves, the angle varying with the wave-length and the temperature. The only colour complication with rhombic crystals, as regards their biaxial interference figure in white light, is, therefore, that due to this cause.

Figs. 686 and 687 on the adjoining Plate V. are reproductions of the author's photographs of the interference figures shown by a plate of rhombic aragonite cut perpendicularly to the acute bisectrix of the optic axial angle. Fig. 686 was produced when the plane of the optic axes was parallel to one of the crossed Nicols, and Fig. 687 when the Nicols were rotated 45° simultaneously, which is equivalent to the rotation of the crystal plate in its own plane for 45°. The apparent optic axial angle in air 2E of aragonite for sodium light is only 30° 52′, this mineral being distinguished for its small optic axial angle. The dispersion for the two ends of the spectrum is very small, not exceeding a degree.

As an instance of accurately measured dispersion of the optic axes, the true optic axial angle $2V_a$ of potassium sulphate, which has been shown to be orthorhombic in symmetry in Chapters IV. and VIII., is 67° 25′ for red lithium light, and diminishes gradually and regularly as the spectrum is traversed until for greenish-blue F-hydrogen light it has become reduced to 67° 7′. This is a normal case of small dispersion, but there are other cases, even in the same rhombic series of alkali

sulphates, in which the dispersion of the optic axes is very much more considerable. Thus rubidium sulphate exhibits an optic axial angle of 28° 30′ for red Li-light and 47° 30′ for violet G-light, a difference of 19°.

The effect of change of temperature on these two typical cases of small and large dispersion of the optic axes is still more striking. On heating the section-plate of potassium sulphate perpendicular to the first median line to 100° C. above the ordinary temperature, namely, to 115°, the apparent angle of the optic axes in air, 2E, increases by 7°, corresponding to an increase of the true angle $2V_a$ of 4°. On the other hand, for a similar change of temperature the optic axial angle of rubidium sulphate changes so rapidly, and in the direction of diminution, an approach of the axes towards each other, that their separation becomes reduced to zero for each wave-length in succession, beginning with the red, and a uniaxial figure, cross and circular rings, is temporarily produced, at 40° for red Li-light, and eventually even for violet G-light at 65°. After this the rectangular cross opens out again and the optic axes re-separate, but along the direction at right angles to their former one. This interesting phenomenon is called "crossed axial-plane dispersion," as it involves the crossing from one principal plane of the optical ellipsoid to another at the critical point when the uniaxial figure is formed. It is brought about in other cases by a change of wave-length alone, at the ordinary temperature, as in the case of brookite, the rhombic form of titanium dioxide, TiO_2, the apparent optic axial angle 2E for red light being 55° and for yellow light 30°, both in the plane {001}, while that for green light is 33° in the perpendicular plane {010}. In all these remarkable changes in rhombic crystals, however, the median lines remain fixed, for all colours and temperatures, identical with the crystallographic axes and those of the optical ellipsoid, although in certain of the more extreme cases, where the optic axial angle begins by increasing with heat, what was the first median line becomes the second as the crossing point is approached. Indeed, in the very extreme case of cæsium selenate, within 250° of temperature all three axes of the optical ellipsoid, all three crystallographic axes, become the first median line in turn.

In white light, the colour phenomena only involve pronounced broadening of the spectrum rings and the conversion of the dark brushes also into spectrum hyperbolæ, when the crossing of the axial planes is not reached. But when the latter occurs, the colour phenomena are specifically extraordinary and exceedingly beautiful, concave spectrum bands, symmetrical to the axial rectangular directions, being essential features. A special account of these cases will be given in Chapter XLIX., and the general explanation of the whole subject of crossed axial plane dispersion discussed.

Dispersion of the Median Lines. — In the monoclinic system an additional phenomenon is introduced, namely, dispersion of the bisectrices. For only one axis of the optical ellipsoid is now fixed by the symmetry, that which is normal to the unique plane of symmetry of the system. Hence, as at least one of the bisectrices of the optic axial angle must lie in the symmetry plane—in which rotation of the two axes of the ellipsoid

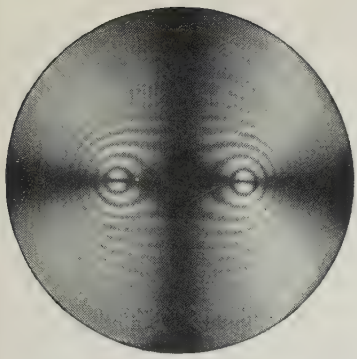


FIG. 686.—Figure given by a Plate of Aragonite (Rhombic) perpendicular to the First Median Line. Nicols Horizontal and Vertical.

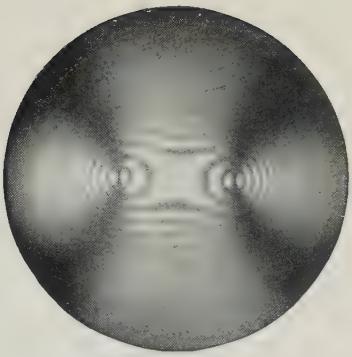


FIG. 687.—Figure given by same Plate of Aragonite when the Crossed Nicols have been simultaneously rotated 45°.

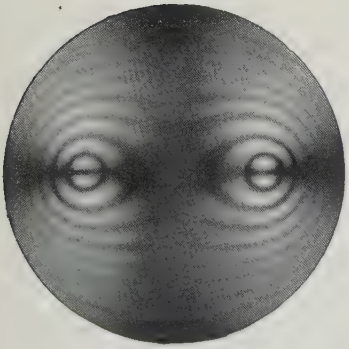


FIG. 697.—Figure given by a Plate of Borax (Monoclinic) perpendicular to the First Median Line. Nicols Horizontal and Vertical.

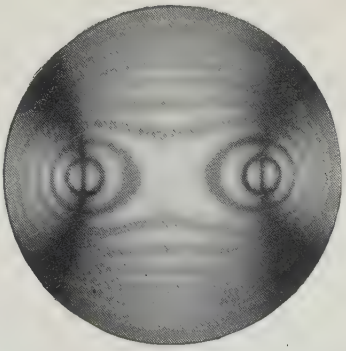


FIG. 698.—Figure given by same Plate of Borax when the Crossed Nicols have been rotated together for 45°.

REPRODUCTIONS OF DIRECT PHOTOGRAPHS OF INTERFERENCE FIGURES AFFORDED BY CRYSTAL PLATES IN CONVERGENT POLARISED YELLOW LIGHT.

Plate to face page 926.

lying in that plane is the general rule whenever the physical conditions, temperature or wave-length of illuminating light, are changed—the position of that bisectrix may be anywhere in the symmetry plane, and will vary under different physical conditions; indeed, when the invariable symmetry axis happens to be the intermediate axis of the ellipsoid, both bisectrices will be in the symmetry plane, and will be equally capable of variation or "dispersion" in that plane, retaining always, of course, their mutually perpendicular relationship. Three distinct cases or types of such dispersion of the median lines are afforded by the possibilities of the conditions in the monoclinic system, and are conveniently known as "inclined," "horizontal," and "crossed" dispersion of the median lines. In these three cases the symmetry axis b of the crystal is respectively the direction perpendicular to the first and second median lines, the direction of the second median line, and that of the first median line.

Case 1, Inclined Dispersion of both Median Lines.—The two optic axes and the bisectrices of the acute and obtuse angles between them in this case lie in the symmetry plane, so that both bisectrices are equally dispersed in that plane, the invariable b-axis being perpendicular to their plane. Hence, if as usual there is also dispersion of the optic axes, one of them will show more dispersion than the other, and as a matter of fact the dispersion of the median lines is measured by observing this difference of dispersion of the optic axes. For if, in Fig. 688, SS represent the symmetry plane, perpendicular to the paper, B the position of the acute bisectrix (first median line) for red light and B′ that for blue, then, when the optic axial angle is larger for violet than for red, as may be conveniently expressed by the symbol $\rho < v$, the angle for red will be RR′ and that for violet VV′. The dispersion of the left axis is then obviously RV, and that of the right axis R′V′, and BB′, the dispersion of the first median line, is the mean of the two, namely, $\frac{RV + R'V'}{2}$; for both axial movements are in the same direction, as represented in Fig. 668. When the two movements are in opposite directions, that is, when the two axes for red are either both within or both without those for violet, the dispersion of the acute bisectrix is equal to half the difference of the two optic axial movements, and in the direction of the larger movement. The mode of carrying out the measurement will be given in detail in Chapter XLVIII.

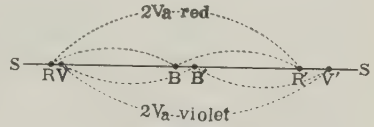


FIG. 688.—Inclined Dispersion of the Median Lines.

Gypsum, $CaSO_4 . 2H_2O$, monoclinic hydrated calcium sulphate, the remarkable crossed axial-plane dispersion of the optic axes of which for different temperatures will be dealt with in Chapter XLIX., is also noteworthy as exhibiting for change of temperature of less than 100° C. inclined dispersion of the median lines of nearly 6°. In an actual experiment of the author's the first median line moved in the symmetry

plane, which is the plane of the optic axes for temperatures up to 91° C., towards the crystallographic axis *c* to the extent of 5° 41′ between 10° and 91° C. The optic axis which moves fastest exhibits the wider rings. It is for this temperature of 91° that the crossing of the axial planes occurs for this same crystal, with production of the uniaxial cross and circular rings.

As illustrated markedly by the extreme case of inclined dispersion exhibited by gypsum, the two series of rings round the two optic axes display a difference in their shape and size, which is more or less accentuated according to the amount of the inclined dispersion. The innermost ring round the one axis is often nearly circular, while that around the other is elliptical. Figs. 689 and 690 will render this clear, for the two positions in which the section is respectively parallel and at 45° to the planes of polarisation of the Nicols. The dotted line PP represents the direction of vibration of the polarising Nicol, and AA that of the analysing Nicol. It will also be seen from the figures that the distribution of colour about the rings when white light is employed is

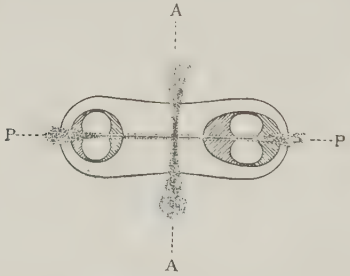


FIG. 689.

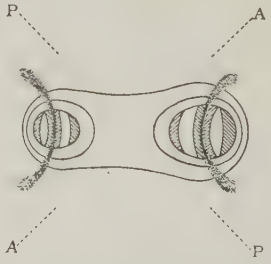


FIG. 690.

Shapes of Optic Axial Rings and Distribution of Colour in Cases of Inclined Dispersion.

symmetrical to the horizontal line (parallel with PP in Fig. 689), the trace of the symmetry plane.

Case 2, Horizontal Dispersion of the First Median Line.—In this case the plane of the optic axes is perpendicular to the symmetry plane, and the second median line is the immovable symmetry axis *b* of the crystal; but the first median line lies in the symmetry plane, and is, therefore, capable of dispersion in that plane. Regarding the interference figure, as usual, through a section-plate cut for sodium light perpendicularly to this acute bisectrix, and with the planes of vibration of the Nicols parallel to those of the crystal, the figure is observed in white light to be laterally symmetrical, but not so above and below the horizontal axial line, as will be clear from Fig. 691. The next illustration, Fig. 692, shows the laterally symmetrical but vertically unsymmetrical arrangement of colours at the diagonal 45°-position of the plate. On illuminating with the spectrum colours in succession, and adjusting the section first so that for one extreme, say red, the horizontal bar of the figure is coincident with the horizontal cross-wire, as at RBR′ in Fig. 693, this bar will be observed to travel parallel to itself

vertically up or down, the optic axes remaining symmetrically placed with respect to the vertical line, the trace of the symmetry plane, but at an altering angle, say VV′ for violet light; the bisectrix B thus moves in the symmetry plane to B′, and the dispersion consists of the displacement

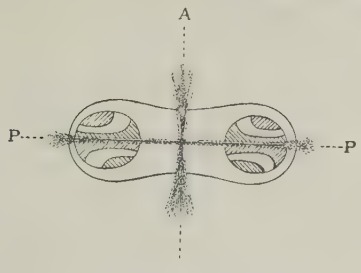


FIG. 691.

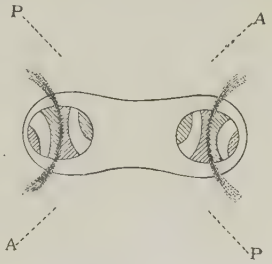


FIG. 692.

Shapes of Optic Axial Rings and Distribution of Colour in Cases of Horizontal Dispersion.

of the horizontal bar RBR′ to VB′V′, assuming the plate to be parallel to the Nicols, while the vertical transverse bar remains on the vertical cross-wire. The character of the dispersion is, therefore, said to be "horizontal." The interference figure in white light is correspondingly unsymmetrical to the horizontal cross-wire, but symmetrical to the vertical wire.

An excellent example of this type of dispersion is afforded by sanidine felspar. Muscovite mica is also another example, reproductions of photographs of the figures given by which in the parallel and 45°-diagonal positions and in yellow light have already been given in Figs. 676 and 677 on Plate IV., facing page 920.

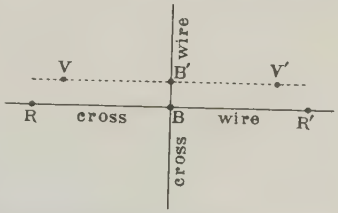


FIG. 693.—Horizontal Dispersion of the Median Lines.

An example of the mode of measuring this type of dispersion will be given in Chapter XLVIII.

Case 3, Crossed Dispersion of the Second Median Line. — In this case the *b* axis of symmetry is the acute bisectrix, and is thus immovable, while the obtuse bisectrix lies in the symmetry plane and is dispersed therein. The plane of the optic axes is perpendicular to the symmetry plane. The interference figure in white light is unsymmetrical to any line, but symmetrical to the centre, where the symmetry axis identical with the first median line emerges, the optic axes themselves being dispersed but not the median line.

If the circle in Fig. 694 represent the symmetry plane, and RR′ the optic axes for red light, then these will be displaced for violet light to a position such as VV′, likewise symmetrical to the centre but along a line inclined to the horizontal more or less according to the amount of the crossed dispersion of the second median line. The kind of distribution of colour (centro-symmetrical) will be clear from Figs. 695 and 696.

An excellent example of this kind of dispersion of the median lines is afforded by borax, $Na_2B_4O_7 . 10H_2O$, reproductions of direct photographs of the interference figures of which in yellow light and for the parallel and 45°-diagonal positions are given in Figs. 697 and 698, the two lower figures of Plate V., facing page 926. These photographs, as in the similar cases of those of mica given in Figs. 676 and 677 of Plate IV., facing page 920, being taken for a particular colour of light, do not show the distribution of colour, but give a clear idea of the shape of the rings. The colour scheme, however, is well shown in Figs. 695 and 696. The optic axial angle in air 2E for borax in sodium light is 59° 23′, an angle intermediate between that of aragonite (30° 52′) illustrated in Figs. 686 and 687 on Plate V., facing page 926, and that of mica (75°) as photographed in Figs. 676 and 677. These three pairs of figures thus illustrate a typically graduated series of optic axial angles of biaxial crystals, as seen in air.

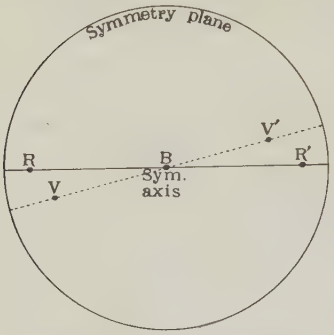


FIG. 694.—Crossed Dispersion of the Median Lines.

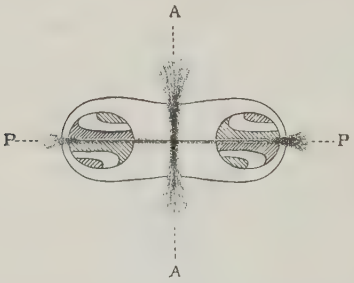


FIG. 695.

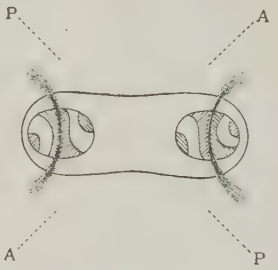


FIG. 696.

Shape of the Optic Axial Rings and Distribution of Colour in Cases of Crossed Dispersion.

The mode of measuring the amount of crossed dispersion will be described in Chapter XLVIII.

Hyperbolic Interference Curves. — A plate of a uniaxial crystal cut parallel to the optic axis usually affords interference curves of hyperbolic character. Fig. 699 reproduces photographically the effect afforded by a plate of quartz so cut. A thinner plate of calcite parallel to the axis also yields curves almost exactly like those in Fig. 699; a calcite plate of the same thickness as a quartz plate always shows the hyperbolæ more closely congregated together. In Fig. 700 is shown an interference figure also composed of hyperbolic curves, afforded by a plate of calcite cut from a natural twin at an angle of $22\frac{1}{2}°$ to the optic axes. This figure is more extended along the direction of one of the planes of the Nicols than along the other, whereas Fig. 699 is symmetrical.

Both figures were obtained when the plate was arranged with its planes of vibration at 45° to the planes of the crossed horizontal and vertical Nicols. (See also page 1126.)

Savart's Bands.—When two plates of quartz or calcite are cut at 45°

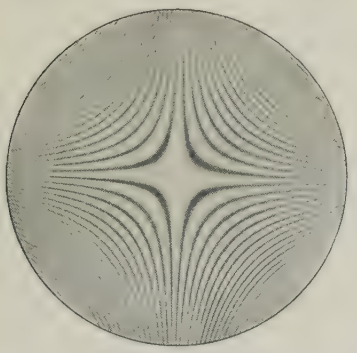


FIG. 699.—Hyperbolic Curves given by Plate of Quartz parallel to the Axis.

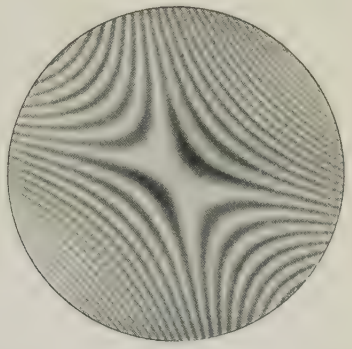


FIG. 700.—Hyperbolic Curves given by Plate of a Calcite Twin cut 22½° to Optic Axis.

to the axis, and then crossed and cemented with balsam at right angles to each other, the composite plate exhibits the parallel bands shown by photographic reproduction in Fig. 701. They are known as "Savart's

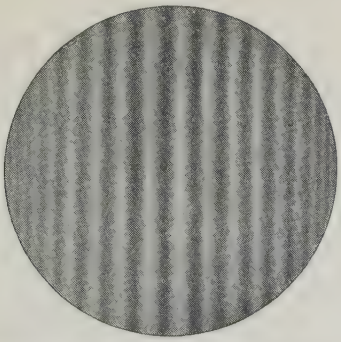


FIG. 701.—Savart's Bands afforded by two Plates of Quartz cut 45° to Axis, and crossed at 90°.

Bands," as Savart employed the device for the construction of an analyser, the double plate affording an extremely delicate test for small amounts of polarisation of light. For only a very slight amount of polarisation in the light reaching such an analyser at once renders the bands visible.

CHAPTER XLIII

THE CUTTING AND GRINDING GONIOMETER

This instrument, with which all the section-plates and 60°-prisms employed in the author's investigations have been prepared, is shown in Fig. 702. It was devised in order to replace by a method of precision the difficult, wearisome, and at the best only approximate, current method of grinding by hand, upon a slightly convex plate of ground glass lubricated with oil or a solvent for the crystal substance, the section-plates and prisms of the relatively soft and fragile crystals of artificial preparations which are required for the determination of the optical constants. It is equally capable of preparing such surfaces, however, on the harder crystals of naturally occurring minerals.

It is possible by means of it to cut or grind and polish a truly plane surface in any desired direction in a crystal accurately to within three minutes of arc, an amount of possible error which would exercise no appreciable influence on the values of the optical constants. This result may be achieved in a small fraction of the time hitherto required by hand-grinding, and, owing to the provision of a delicate arrangement for suitably modifying the pressure with which the crystal bears on the grinding plane, with only the very slightest risk of fracturing even a friable crystal. An automatic time-saving device is also provided, by which a second surface may be ground parallel, with a like degree of accuracy, to the first. Moreover, there is a special apparatus for preparing the two faces of a 60°-prism with only a single setting on the crystal-holder. The section-plates and prisms of non-perishable substances furnished by the instrument possess the further advantage of being so highly polished as to enable them to be employed in most cases directly, without cemented cover-glasses, for the determination of the refractive indices and optic axial angle. Even in the cases of the more perishable ground and polished faces of the crystals of chemical preparations, especially those of salts containing water of crystallisation, the author has proved by an exhaustive series of actual determinations that, when the following three precautions are taken, thin cover-glasses may be used permanently to protect and preserve the prepared surfaces without any appreciable effect on either the refractive index (expressed to the fourth decimal place) or the optic axial angle. These precautions are :

(1) Only thin micro-cover-glasses should be used which have been tested on the goniometer and proved satisfactory as regards true-planeness and parallelism of their two surfaces; (2) the pieces used, cut by a diamond

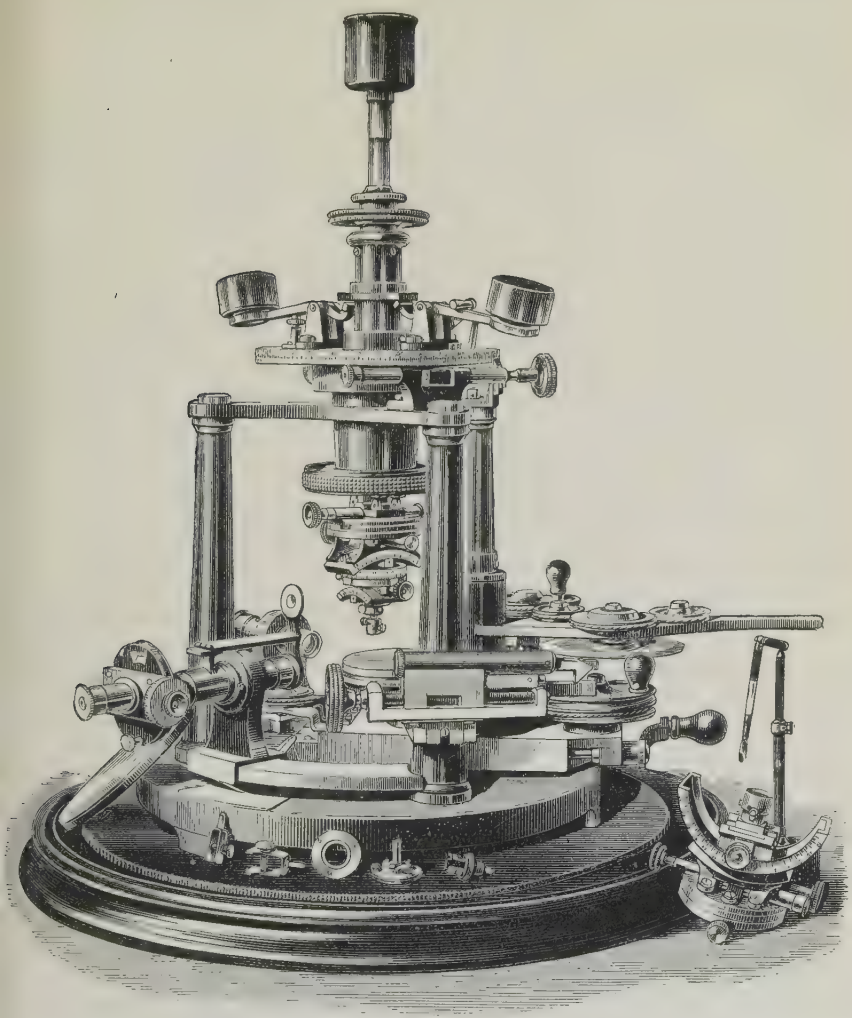


FIG. 702.—The Cutting and Grinding Goniometer.

from such truly plane-parallel cover-glasses as have passed the test (1), should scarcely exceed in size the dimensions of the ground and polished facets on which they are to be mounted, however minute these may be; and (3) the mounting of the miniature glass plates should be effected with the minimum of hard Canada balsam dissolved in benzene, so that on drying by evaporation of the benzene the cementing layer shall be a very

thin and parallel surfaced film. The values of these constants derived from prisms and section-plates prepared with this instrument are thus no longer only approximate but precise.

The instrument consists essentially of six parts: (1) an accurate goniometer of the suspended type with horizontal circle, provided with (2) adjusting movements for the crystal, furnished with divided circles and of special construction; with them are combined (3) a crystal-cutting gear and (4) a separate crystal-grinding and polishing gear, (5) an apparatus for controlling the pressure with which the crystal bears on the lap, and (6) a variety of crystal-holders specially constructed for the different objects in view, and affording considerable means of preliminary adjustment.

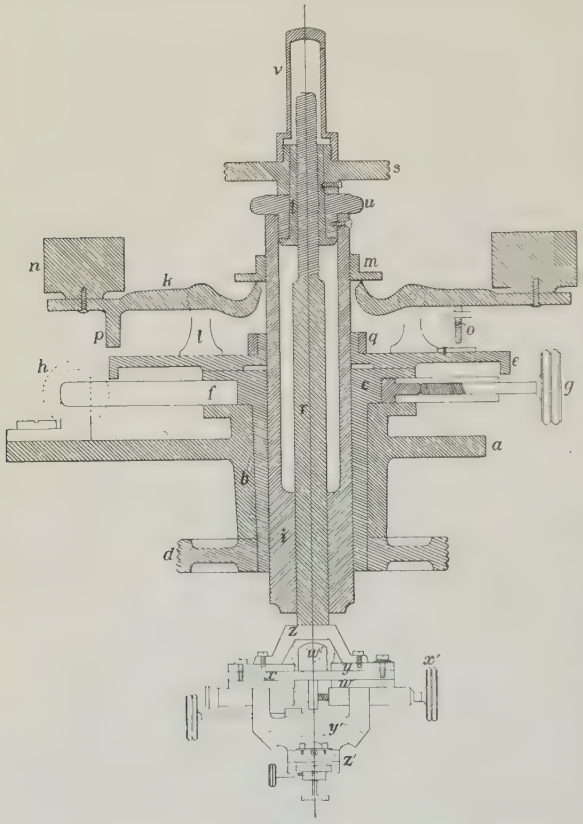


FIG. 703.—Section of Axial System of Cutting and Grinding Goniometer.

The goniometer circle and adjusting movements are supported at the convenient height above a heavy circular base by three stout pillars and a triangular cross-plate, the latter lettered *a* in the section given in Fig. 703. The central bearing cone *b* for the various axes is part of the same casting with the cross-plate, and within it rest in succession three movable inner axes. The construction of these will be rendered clear by the section, Fig. 703, to which all the letters in this description refer. The first *c*, which may be rotated by a milled ebonite wheel *d*, carries at its upper end the horizontal circle *e*, which is directly divided into half-degrees and reads with the aid of a vernier to single minutes. It is provided with a fine adjustment *f*, and fixing-screw *g*. The milled head of the fine adjustment screw is indicated at *h* in Fig. 703 and is seen in front in Fig. 702.

The bore of the circle axis *c* is cylindrical, and within it the second movable axis *i* is capable of vertical motion only, rotation being prevented by a rib and groove. This axis *i* is designed entirely for the purpose of modifying the grinding pressure

between crystal and lap. The whole weight of the axis and all that it carries may be wholly or partially counterbalanced by a pair of levers *k*, the fulcrum supports *l* of which rest upon the circle plate *e*. Their inner and shorter curved arms terminate in blunt knife edges which press upwards against a collar *m* carried by the axis *i*, and which is adjustable to any convenient height; their power-arms are weighted by leaden weights *n*, which together counterpoise the whole weight. One of the levers, the right one in Fig. 703 and left one in Fig. 702, may be thrown out of action by raising a capstan screw *o*, thus leaving half the weight of the axis only in operation. The author generally employs the axis so, manipulating the free lever with the left hand, lightly holding the counterpoise *n* between the thumb and two fingers, and manipulating it according to the "feel" of the grinding. A spur *p* prevents the axis being raised inconveniently high. In the cases of very soft artificial crystals the screw *o* can be lowered and thus both levers rendered available in reducing the pressure. On the other hand, when hard mineral crystals are being dealt with, the weight on this axis *i* can be increased by placing small shot or weights in a brass cup carried at the upper end of the axis, its stem fitting over the cylindrical cover-cap *v* indicated in section in Fig. 703, as shown in position in Fig. 702. These arrangements thus enable the weight above the crystal to be varied during grinding or polishing to any desirable extent. The use of the left hand on the left lever enables the most delicate control to be maintained over the pressure on the lap, and after a little practice it is an extraordinary occurrence that a crystal should break or crumble under the operations. The axis *i* can be fixed rigidly to the circle (the latter being previously fixed by the clamping screw *g*) by means of the gripping collar *q*, the screw of which is tightened up by a key provided. This fixation is necessary during cutting operations. During adjusting operations it is not necessary to keep the axis *i* up by this fixation, a little locking hook being simply thrown over the longer arm of that lever which is usually manipulated by the left hand, but rotated to the right in Fig. 702.

Within this second axis *i* slides, also without rotation owing to keying, the third axis of steel *r*, which carries at its lower end the crystal and its means of adjustment. The upper portion of this axis is tapped with a fine screw thread, and the axis can be raised or lowered by a milled-headed wheel *s*, which manipulates the driving-nut *t*. The latter rotates without vertical motion within the solid head *u* of the hollowed axis.

The crystal-adjusting and centring apparatus is carried at the lower end of the inner steel axis *r*, and consists of the usual two circular adjusting segments and pair of horizontal centring movements, but is constructed more strongly than usual. The centring is attained by the movement of two circular discs *w* and *x* about each other by means of a pivot near the periphery, and of these two about a third *y* in a similar manner, which latter is rigidly fixed to the lower end of the steel axis *r* by means of the bridge *z*. The movements are maintained steady by a slot and screw with large head in each case, near the periphery at the opposite side of the centre to the pivot. The end of the centring screw *w'* or *x'* presses against a short vertical piece fixed to the central disc *x*, and passing through a central hole in the outer disc *w* or *y*, contact between screw and upright being maintained by a spring piston pressing on the other side of the upright. The two movements are arranged at right angles to each other. The adjusting movements are the two circular movable segments *y'* and *z'*, rotated over strong cylindrical guiding beds by a couple of tangent screws with milled heads, arranged, like the movements, at right angles to each other, particular care having been taken to set both at exactly 90° 0′. The screw which rotates *y'* is shown to the left in Fig. 703. The movements differ from those of an ordinary goniometer in being provided with silver scales divided directly to degrees, on the faces of the guiding beds, and with silver indicator-marks to correspond on the movable segments. The tenth of a degree of movement may readily be set, and a twentieth (3′) estimated.

Besides this pair of circular motions of which the two planes are fixed at right angles, an alternative set is provided, shown both in position in Fig. 702 and in Fig. 704, in which

the lower movement may be adjusted at any desired angle to the upper movement, by means of a horizontal circle with silver scale, also divided directly into degrees, carried by the upper movement, the lower movement carrying on a similar circle plate four indicating marks on silver 90° apart. The lower movement may be clamped to the upper one in any position by means of a double tightening screw, which fixes the indicating disc to the circle, and which can be manipulated from either side by means of a key supplied.

The crystal is to be attached to the small cross-grooved disc of the crystal-holder by hard and rapidly-setting optician's wax; as used by the author, this is composed of the best British pitch, hardened by long boiling, purified by straining, and admixed with more or less fine rouge. It is to be adjusted so that the zone of faces perpendicular to which it is desired to grind a surface, if such a zone be developed, is parallel to the vertical axis. When a zone of this character is not present, as will

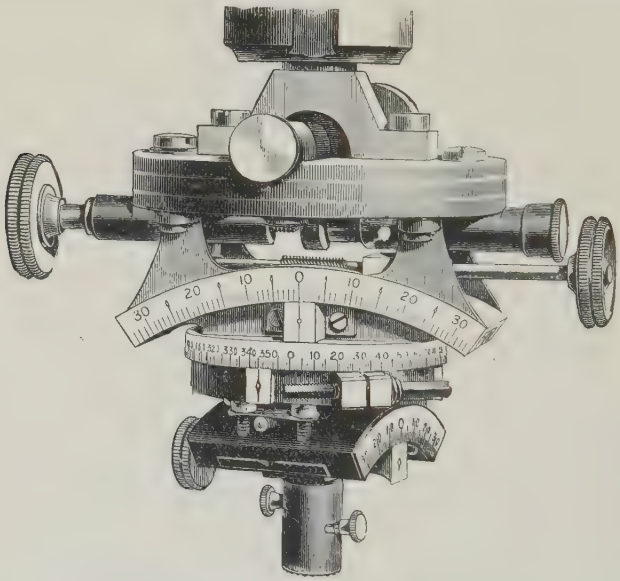


FIG. 704.—Special Crystal-adjusting Movements of Cutting and Grinding Goniometer.

happen in monoclinic and triclinic crystals, a prominent one of convenient and accurately known position with respect to the surface to be ground is adjusted, and with the aid of the two circular movements—arranged either at 90°, or at any other desirable angle if the crystal be triclinic—the calculated necessary rotations can be given to bring the plane in question within the crystal parallel to the grinding lap. For all ordinary cases up to and including monoclinic crystals, the author prefers to use rectangularly fixed movements, and in order that the desired plane shall be adjusted for grinding or cutting it is usually only necessary to rotate one of the movements for some particular angle — indicated by the extinction determinations — after the prominent zone has been accurately adjusted, and after one face has been set either parallel to one of the movements or at some definite angle with it. Provision for setting any face exactly parallel to a circular motion is provided in a series of special crystal-holders of graduated sizes to suit different sized crystals, which permit of the requisite amount of rotation after the holder is fixed in its socket. Two different ones are shown in position in Figs. 702 and 704 respectively. The cross-grooved attaching-plate forms the bottom of a hollow cylinder, which is rotatable about a

solid cylindrical core, and capable of fixation in the adjusted position by two screws passing through slots of adequate length to permit of over 45° of adjustment. A very small glass plate, cemented on the side of the adjustable segment strictly parallel to the plane of its circular movement, is used to obtain a reflection of the collimator signal-slit, and for the allocation of this image to the cross-wires of the telescope the circle reading has once for all been determined, thus enabling the setting of the face to the same reading by means of the adjusting cylinder to be accurately attained. In Fig. 703 one of the unadjustable holders is shown. In addition, three gripping holders are also provided, shown resting on the wooden basal plinth of the instrument in Fig. 702, over which fits the protective glass shade. All are padded within their prongs with cloth; two are merely of the pincette type, while the third is triply split, and the three prongs are tightened when gripping a crystal by working down an annular nut upon them, the upper part of the stem being tapped with a screw thread. All the crystal-holders fit by means of a central peg into an axial hole in the lower adjusting segment, and can be fixed there by a tightening collar (Fig. 702) or fixing screw, the lowest visible in Fig. 703.

For **grinding the parallel surface of a section-plate**, after the first surface has been prepared, a further special crystal-holder is provided, consisting of two parts screwed together, one being like a shallow cap and the other a disc with central peg. The two parts are shown, separated, lying in front on the wooden base in Fig. 702. The crystal is mounted by its already ground surface on a circular disc one centimetre in diameter of truly parallel glass, with hard Canada balsam dissolved in benzene. This is laid, when the balsam is quite dry and hard set, in a concentric rabbeted receptacle for it in the centre of the cap-like part of the special holder, with the crystal projecting through. This part is then fitted to the other, which consists of a thick metallic disc one inch in diameter; one surface of this disc is a true plane, and the other carries in its centre and perpendicular to the true plane the usual insertion peg, and also an enveloping cover-plate very similar to the cap. The disc fits nicely into the circular depression in the cap, and the latter bears three little screw-tapped uprights at equidistant positions on its marginal flange, which fit through holes in the cover-plate, so that when little milled nuts are screwed on the three screws the two parts are firmly fixed together, with the glass plate pressed into full contact with the true plane. This true plane should previously have been adjusted—when placed in position with the peg (which has a groove fitting a pin in the socket, to prevent rotation and enable it always to regain a similar position on insertion) in the socket at the bottom of the crystal-adjusting apparatus—so that it is absolutely parallel to the grinding lap. This is readily ascertained by lowering it close to the lap and adjusting till an evenly thin line of light is seen between the two in all positions on rotation of the crystal axis. It will then recover this parallel position on reinsertion after attaching to it the lower part containing the section and its glass-plate mount by means of the three screws. As the rabbeted annulus holding the glass plate is very thin, a section may be ground which may, if required, be almost as thin. The cap is made of very hard white metal in order that the thinness of section-plate may be as extreme as is ever required, in the cases of crystals of high double refraction. The second surface thus ground is bound to be parallel to the first, as the glass plate on which it is mounted is parallel-surfaced, and the surface of the true plane, itself parallel to the grinding lap, is in absolute contact with it. The disc with its cemented crystal may be removed from time to time during the grinding without disturbing the adjustment, so that grinding may be stopped when the section is of the desirable thickness to enable it to exhibit small rings in its interference figure, the condition required for measurement of the optic axial angle; or whenever any other desired thickness, to suit some other condition or experiment, is attained.

In order **to prepare a 60°-prism**, that is, two surfaces inclined at 60°, by one setting of the crystal on the wax of the holder, it is obviously necessary to rotate the crystal

for 60° on each side of the particular principal optical plane which has been adjusted vertically to the grinding plane, with the aid of the goniometrical arrangements provided on the instrument, and to which optical plane the two required surfaces are to be symmetrical. The two cylindrical movements of the ordinary adjusting apparatus already described admit of 35° of rotation on either side of the vertical axis in each case; this amount is ample for all the purposes of the preparation of section-plates, and also for the preparation of a 60°-prism by separately setting the direction of each required prism-face, by rotation of 30° from the plane perpendicular to the bisecting plane, which can usually be as readily adjusted as the bisecting plane itself. But it repays to render the adjusting mechanism more cumbrous in order to achieve both surfaces by one setting; hence, a special alternative adjusting apparatus is provided for this purpose. It is shown in Fig. 702 in the immediate foreground, to the right.

A duplicate centring arrangement is given with it, so that it is only necessary to detach the whole of the ordinary apparatus from the bottom of the steel axis *r*, by unscrewing the four screws attaching the upper centring disc to the bracket (*z* in Fig. 703), these screws in the latest form of the instrument (Fig. 702) having milled heads and also capstan holes, for more rigid fixation by a steel lever provided. The new attachment is exactly like the ordinary movements down as far as the upper fixed cylindrical segment and its divided silver scale reading 35° on each side of the indicator-zero. But the movable segment sliding within it is made double the usual size, that is, of rather more than 150°. On one face, immediately below the fixed scale, it bears at the centre an indicating mark on silver for that upper fixed scale, while on the other face it bears a silver arc graduated to 75° on each side of the centre. This large movable segment is only movable as regards the 35° of adjustment, and is usually only moved for the few degrees required for the adjustment of the bisecting plane of the proposed prism; it is thus the fixed segment as regards the large rotation for the two faces to be ground. Within it, underneath, the usual lower adjusting movement of the ordinary kind slides to the large extent of 75° on each side already indicated, the plane of the two movements being in this case permanently fixed at 90° in order to save further unnecessary complications. The adjusting movement of the large segment about the upper fixed one is effected in the usual manner, by tangent screw, for the 35° of its path on each side, indicated by the upper ordinary scale. The lower rectangular movement is similarly supplied with a tangent screw. But the large amount of sliding of the carrier of this lower movement for the grinding of the two prism-faces, within the large new segment, is effected by hand, and fixation at any required position with reference to the large silver arc can be brought about by a milled-headed screw-clamp on the opposite side to the index and lower tangent screw.

In using the apparatus, the crystal is attached by the minimum of wax to the smallest of the adjustable cylindrical crystal-holders, so that the proposed bisecting plane of the desired 60°-prism is arranged vertically, as nearly parallel to the goniometrical axis as possible, and parallel to the lower tangent screw. The azimuth adjustment of the crystal-holder is very useful in attaining this. Exact adjustment of the plane in question is then perfected with the two tangent screws, and so that the direction of the desired refracting prism-edge is brought truly parallel to the grinding lap-surface, the clamping screw being meanwhile fixed with the indicator on the large arc at zero. The screw of the clamp is then unloosed and the slider with the lower movements and the crystal moved round 60° on one side, as indicated by the silver index against the large arc, and the clamp again fixed. The first surface may then be ground and polished. The clamp is then again loosed, the lower part of the apparatus rotated back to zero and further to 60° on the opposite side of the centre, the clamp fixed, and the second surface ground and polished.

The **goniometrical telescope and collimator** are arranged in the horizontal plane at the convenient height for observing the crystal. They are movable over circular guiding arcs, the centre of which lies in the vertical axis of the instrument. This

adjustment can be perfectly attained once for all by means of three adjusting screws passing through collars round the optical tubes into the corresponding bearing supports; a strong annular spring is confined between the collar and bearing in each case and presses them asunder, while the three adjusting screws at 120° intervals draw them together against the force of the spring, which is so strong as to afford a very rigid adjustment.

A combined goniometer- and micrometer-eyepiece is provided, due to the suggestion of Sir Henry A. Miers; it has two fixed spider-lines at 90°, one adjusted exactly parallel to the vertical axis of the goniometer and the other horizontal, and a third spider-line which is both rotatable and capable of movement parallel to itself in the focal plane. The fixed lines are attached in the central aperture of a circle-plate 7 centimetres in diameter fixed round the optical tube of the eyepiece, and which carries near its periphery a circle divided into degrees. The movable spider-line is arranged in the aperture of a micrometer-box carried in front of a similar circular plate, fitting closely to the first plate and partially enveloping it with a milled flange so as to be rotatable about it. A window through this front plate, seen above the micrometer in Fig. 702, allows the circle to be read through it, the inner edge of the window being bevelled and engraved with a vernier, by which the circle can be read to minutes. The movable spider-line is fixed to the traversing frame of the micrometer, at the focus of the Ramsden eyepiece, which slides in a short front tube. By a suitable device the fixed lines are brought also into the focal plane and almost in contact with the movable line. The traverse of the latter and its frame is recorded by a drum on the right, divided into 100 parts, the reading being by an indicator alongside. The two circles can be clamped together, when desired, by the fixing screw seen below the micrometer in Fig. 702.

These arrangements on the telescope enable the instrument to be used not only for its specific purpose, but also for the study of small movements of the image of the collimator signal-slit, which in this instrument is of the kind shown in Fig. 26 (p. 44), reflected from a crystal face during the growth of the crystal in a cell of mother-liquor placed on the grinding-table, and due to disturbance of the thermal or other conditions of the solution. In fact this instrument serves for a most useful variety of other purposes than that for which it was primarily designed, particularly for the determination of refractive indices by the total-reflection method, as will be found described in Chapter XLVII., and is a most valuable acquisition to a crystallographic laboratory.

The removable lens in front of the telescope objective is capable of being thrown into position as usual for the purpose of converting the telescope into a low-power microscope, or a duplicate may be placed in front of the eyepiece and made to travel for some distance in front of the latter along the optic axis, in order to follow any signal-image right up to the image of the crystal face reflecting it. The pair of lenses are mounted for this purpose on the cross-bar of a T-piece, the stem being hinged to a short upright from a tube sliding without rotation over the main optical tube. This arrangement is of considerable value in tracing the images derived from vicinal faces; such vicinal faces may be actually studied during the growth of the crystal, by the method employed by Sir Henry Miers (see p. 393, Chapter XXIV), to whose suggestion this accessory is also due.

Just below the plane of the optical tubes the **horizontal grinding table** or "lap" is supported, in a frictionless bearing carried by an adjustable dovetailed slider moving over a correspondingly dovetailed guiding bed. Ten interchangeable laps of different materials are provided, to suit the grinding and polishing of crystals of every degree of hardness. There are three glass laps, two of which are respectively very finely and moderately finely ground, while the third is polished clear; there are four metallic laps, of iron, gun-metal, hard white-metal, and pewter respectively, for use with emery, putty-powder, rouge or rottenstone and water; another lap is of boxwood, for use with putty-powder in polishing, and a further polishing lap is of hard optician's

wax, mounted in a metallic tray, for use with rouge as in polishing glass surfaces; the tenth is an emery wheel. Over any one of the metallic laps may be stretched emery cloth, chamois leather, broadcloth, satin, parchment, or any other fabric or integument which it is desired to use for grinding or polishing purposes; and two interchangeable bronze rings, of different tightness of fit, are provided to encircle the laps and secure the covering material in its tightly stretched condition (affording a flat surface) over the lap. Security is also aided by six little pressure screws with milled heads, screwing through the ring.

The surface of each of these laps is made a true plane, and any one can be fitted on the permanent supporting table of the same diameter (4½ inches) at a moment's notice, fitting by three pegs into corresponding holes in the table, and being simply locked there by rotating a little lever under the table, which brings a locking-plate into grooves in the pegs. The glass laps are employed chiefly with the crystals of artificial salts, one of the two ground-surface laps being used for grinding, lubricated with "brick" oil (olive oil in which a red-hot brick has been plunged, which appears to destroy certain clogging constituents), or in some cases only with the moisture of the breath; the clear plate-glass lap is used for polishing, lubricated in a similar manner.

The lap is rotated by a driving gear arranged equally on each side of the axle so as to diminish strain, the driving pulley being on the right and a friction pulley on the left. The grinding is best under control when the driving pulley, which is provided with a suitable handle, is rotated by hand, each revolution producing two revolutions of the grinding lap. The driving pulley is, however, provided with two grooves, the upper of which is intended for the reception of a band from an electric motor, whenever power driving can be safely employed.

Concentric grooving of the lap is avoided, and more or less equal wear ensured, by the mounting on the slider, which is made to traverse the dovetailed bed resting on the circular iron base of the instrument by rotation of a long driving screw gearing with a thread in the bed and manipulated by a winch handle at the right-hand end. The inner end of the screw being unflanged, the slider and all that it carries can readily be removed altogether after driving outwards to the end of its path, in order to afford more room when the cutting apparatus is in use. The permanent table on which the laps are interchangeably mounted is provided with the means of adjustment by three strong screws, which level its axle base-plate with respect to the slider, in order to be able to bring the table exactly perpendicular to the vertical goniometrical axis. The friction pulley is also adjustable by means of slots in its bearing-bracket, through which its fixing screws pass, so as to be able to tighten the driving band. Any friction of the band may also be entirely avoided, as both driving and friction pulleys are so mounted that they may be slightly tilted if desired, three-screw adjustments being provided for the purpose.

An adjustable guard-screen is also provided to protect the observer and the optical parts of the instrument from splashing during the cutting or grinding of hard crystals. It is very seldom required, however, as splashing rarely occurs with brick oil as lubricant, in the cases of the small crystals generally operated on for crystallographic optical investigations. It is never required for use with the glass laps and artificial chemical crystal preparations.

The **cutting apparatus** is carried at a height which brings the diamond-fed cutting disc of soft iron, 4 inches in diameter, to exactly the same level as the grinding surface of the lap. It is separately mounted on a rigid horizontal arm pivoted on the back pillar of the instrument, so that it can be rotated out of the way during grinding operations. It is further supported when required for use upon an adjunct of the right front pillar. The cutting disc is supported between two stout broad washers carried by the frictionless axle, and is driven by an independent gear also mounted on the arm, consisting of a driving pulley and two friction pulleys on opposite sides of the axle. The driving pulley is given in duplicate, the second one being below on the

same axle, and intended for motor driving when desired. The arm on which the whole apparatus is carried is bent inwards towards the crystal, in order to advance more conveniently the cutting diamond-edge of the iron disc to the crystal. Three interchangeable cutting discs are provided, one of the usual thickness of a lapidary's cutter, and two somewhat thicker and therefore more rigid. Their edges are charged with diamond dust (a diamond being crushed in a steel mortar to provide it) by smearing a mixture of oil and the dust round the edge and then forcing it into the soft iron by holding a piece of agate against the disc during its rotation. After one or two repetitions of this treatment the cutting edge of the disc becomes charged with enough diamond to last for years. The edges of all the discs had first been carefully squared (made perpendicular to the surfaces of the discs).

The support for the arm on the front pillar is a fitting which is instantly removable, by sliding upwards out of a dovetailed grooved bearing, the latter forming a permanent part of the pillar; the fitting is always thus removed during grinding operations. The sliding dovetail, which forms the back portion of the removable fitting, slides immediately into position in the recess, a stop arresting the fitting when at the right height. The attachment includes not only a supporting fork for the arm (somewhat like a tuning-fork placed horizontally), but also the apparatus for directing and controlling the cutting. The latter consists of a horizontal traversing bed and slider, manipulated by the large milled head of the traversing screw seen in front of the centre in Fig. 702. The arm is attached to the slider by being gripped between a small spring piston and a spring-hinged wedge-shaped hook in front of the fork; the hook is pushed out of the way by the arm in entering the fork, but is caused to slip back behind the arm by the spring pressing it down from above. This gripping arrangement is carried by a much larger piston, retained by a strong spring in a cylinder fixed to and above the slider. The possibility of undue pressure being developed between cutter and crystal, owing to injudiciously rapid rotation of the traversing screw, is thus avoided; for the spring gives way before the pressure becomes dangerously great, the piston being pulled out of the cylinder. Two inches of traverse are permitted by the length of the fork and of the traversing bed of the slider, an amount ample to permit of the cutting through of a crystal nearly an inch in diameter, a size never exceeded and rarely approached in work of the character contemplated with the instrument.

This form of cutting apparatus is found to work admirably. There is no tendency to jamming when once the operator has become familiar with the rate at which the milled head of the traversing gear can most advantageously be rotated with the left hand, while the driving wheel is manipulated with the right; and the cutting is more perfectly under control than when the pressure of the cutter is brought about by a spring or a weight hanging over a pulley.

In order to cut through a crystal along a specific plane, the latter is first adjusted parallel to the plane of the optical tubes, and therefore to both the cutting disc and grinding lap, by the goniometrical means already described. The crystal is then lowered by rotation of the milled head at the top of the instrument until it is at a convenient height for cutting, in which position it is fixed by first clamping the circle to the fixed cone by the milled-headed screw forming part of the arrangement for fine adjustment of the circle (at the back of the circle in Fig. 702, *g* in Fig. 703), and then preventing any movement of the balancing axis *i* by tightening the collar *q* immediately above the circle, by means of the key supplied. Cutting is then proceeded with, commencing the rotation of the cutter and its traversing very slowly at first, and gradually increasing the speed according to the "feel" of the cutting, the diamond wheel being lubricated with brick oil. If by inadvertence a jam should ever occur, the slightest reversal of the motion of the traversing screw will instantly release the cutter. The speed should be materially reduced towards the finish, in order that the end of the crystal may be cut off cleanly right up to the farthest edge. A hard crystal such as a topaz (hardness 8) may be cut through in a very few minutes, and the cut

surface is so smooth that very little grinding is required, which may be at once proceeded with on the gun-metal or hard white-metal lap, with the finest washed flour emery, made into a paste with water or brick oil. A thick glass disc an inch in diameter is provided for use as a "bruiser," to work down the emery paste to an even consistency on the lap before grinding. The cutting apparatus is rotated out of the way to the back, and the front-pillar attachment altogether removed, in order

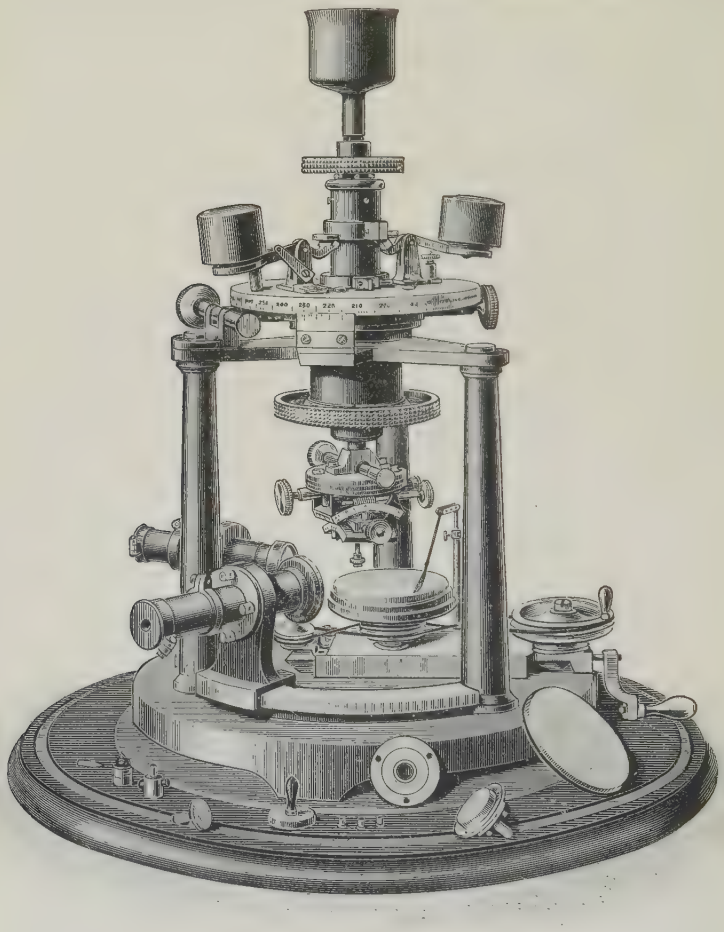


FIG. 705.—The Crystal-grinding Goniometer.

to afford ample room. The pressure between crystal and lap is controlled as already described, by manipulation of the left counterpoised lever with the left hand, and the path of the crystal on the lap changed by moving the slider along its bed more or less from time to time. During grinding, the axis i is, of course, quite free, having been released after the cutting. Polishing may occur exactly as carried out by opticians, with any of the polishing laps already mentioned, which provide for all the current methods of work, except that the crystal is fixed while the polisher revolves.

A further useful accessory is a small adjustable stand, shown to the right in Fig. 702 behind the prism-preparing adjusting movements, to which may be fitted either an oblique caoutchouc wedge, for keeping the emery paste moving into the path of a hard mineral crystal during grinding, or a camel-hair brush, to keep the path in front of a softer crystal of an artificial chemical preparation free from particles of crystal and well supplied with the lubricant.

The glass laps are exclusively used for the preparation of surfaces on such artificial crystals and no grinding or polishing powder is used; also nothing but brick oil or the moisture deposited by breathing on the cold lap is used as lubricant, whichever is found most suitable by experience with the particular substance in hand. The surfaces are in these cases finished on the plate-glass clear lap, as a rule with only a trace of moisture or brick oil on it. Such surfaces, when the crystal is not one of an efflorescing or otherwise deteriorating substance, are usually beautifully polished, and section plates and prisms provided with such surfaces can at once be used for the purposes of measuring the optical constants. If the surfaces rapidly deteriorate they are protected by cementing over them, with hard balsam in benzene, miniature plates of cover-glass, which had previously been optically selected, by reflection tests, as truly plane surfaces in the manner already described.

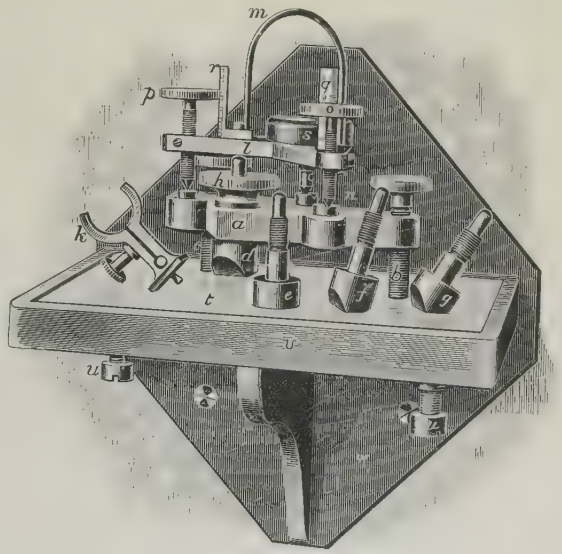


FIG. 706.—Wülfing's Crystal-grinding Apparatus.

In concluding this description of the cutting and grinding goniometer, it may be stated for the benefit of workers only with artificial chemical preparations, for whom the cutting apparatus is unnecessary, that a smaller model of the instrument has also been constructed for the author by Messrs. Troughton & Simms, the makers of the larger model, without the cutting gear, at a considerably less cost. It is shown in Fig. 705. The grinding apparatus and all the rest of the instrument is exactly as described in the preceding pages. This is a remarkably handy and efficient little instrument, and is of the utmost utility to the chemical crystallographer.

The Wülfing Crystal-grinding Apparatus. — An ingenious little apparatus, shown in Fig. 706, for grinding an orientated surface on a crystal has been devised by Wülfing [1] and is constructed by Fuess.

It consists of a small tripod of which the table *a* is a thick plate of aluminium,

[1] *Zeitschr. für Kryst.*, 1890, *17*, 445; *Jahrbuch für Min.*, 1902, *2*, 1.

a somewhat flat isosceles triangle in shape, and cut away in the middle. Two of the feet *b* and *c* are steel screws, and the third is formed by the crystal itself, cemented to a holder *d* of gun-metal, which is one of four interchangeable holders, of different shape at the lower end, the other three *e*, *f*, *g* being shown in front in Fig. 706. The selected one of the four is fixed in position by the milled nut *h*, which gears with a screw thread cut near the upper end of the holder, the middle cylindrical part of which fits in the boring through the table at the angle formed by the two equal sides. One of these holders *e* terminates simply in a flat normal surface, while the other three have each two surfaces meeting in an edge and inclined at various angles, *d* being 10° and 60°, *f* being 20° and 50°, and *g* being 30° and 40°, in order to facilitate the cementing of the crystal in the approximately desired position with respect to the grinding surface.

A surface is first ground on the crystal approximately to the eye in the desired direction, with reference to some well-developed crystal face, and the holder *d*, *e*, *f*, or *g* on which it is mounted is then gripped about its broad cylindrical end by the fitting *k*, a stout pincette supported at right angles by a bracket-plate carrying a central peg, by which it is next attached to the crystal-adjusting apparatus of the Fuess No. 2*a* goniometer instead of an ordinary crystal-holder. The real angle with the crystal face, and thus the error, is then measured on the goniometer. The crystal-holder is then detached from the pincette and fitted to the tripod, and over the latter is placed a second tripod *l* provided with a lifting loop *m*, in such a manner as to rest on three steel supports, the tops of screws, two of which are driven through little projections from the two equal sides as at *n*, and the third driven through the middle of the basal side of the triangle. One of these screw heads has a flat top, another a conical countersunk central depression, and the third a V-groove, so that this second tripod *l* may rest on the main tripod table *a* in the approved method for stable three-point contact.

Two of the legs of this tripod are screws of half a millimetre pitch with sharp conical points and large milled heads *o* and *p*, divided on their flat tops into 12 parts, every second of which is numbered to count as 10, so that the circle corresponds to 60 divisions. Each of these divided heads rotates almost in contact with a vertical scale, *q* or *r*, of half millimetres, to measure the number of revolutions of the screw. The third leg is fixed, after once for all being adjusted to a convenient length, and immediately above it on the table top of this second tripod lies a circular spirit-level *s* of 2½ centimetres diameter. This second tripod *l* is so constructed that each complete rotation of either of the graduated screws brings about an inclination of 1°, the 60 divisions of the screw head thus corresponding to minutes.

With the help of these calibrated adjusting screws and the spirit-level of the upper tripod on the one hand, and the adjusting screws of the lower tripod on the other, it is possible with a little thought and a few trials to correct the crystal surface to the desired direction. The whole apparatus may be mounted on the ground-glass crystal-grinding plate *t*, fitting over three levelling screws *u* in the horizontal table *v* of a cast-iron bracket *w* screwed to the wall of the room or other rigid vertical support.

When it is not possible to incur the expense of the author's cutting and grinding goniometer, or even of the smaller grinding goniometer, which enables the desired surface to be cut or ground and polished right away to the degree of accuracy of a very few minutes of arc, this inexpensive method of approximations of Wülfing, or, better still, the apparatus described in the next section, may well be resorted to.

Crystal-grinding Apparatus of Thomas and Campbell Smith.—An apparatus of somewhat similar type, but a very great improvement on that

of Wülfing, was described in 1914 to the Mineralogical Society by H. H. Thomas and W. Campbell Smith.[1] It is shown in Fig. 707.

The body of the apparatus [2] consists of a triangular brass plate *B* (Fig. 707) surmounted by a brass cylinder *D*, which is graduated on its upper surface into divisions

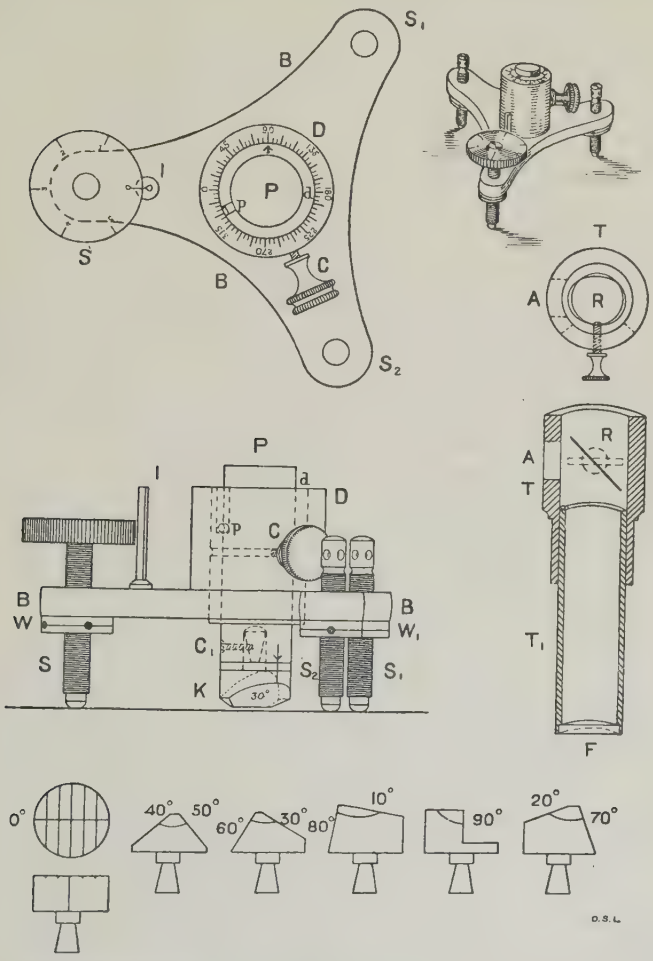


FIG. 707.—Apparatus of Thomas and Campbell Smith for cutting Crystal Plates and Prisms.

representing 5°. This outer cylinder carries inside it another brass tube *d*, which is capable of rotation about a vertical axis; a clamp *C* enables it to be fixed in any position. The centre of the instrument is occupied by a solid gun-metal plunger *P*, capable of independent vertical movement only, and restrained from rotation by a pin *p*, which fits into a slot cut in the rotating tube *d*. The bed-plate *B* of the

[1] *Mineralog. Mag.*, 1914, *17*, 86.

[2] The instrument is constructed by Messrs. James Swift & Son, Ltd., 81 Tottenham Court Road, London, W.

instrument is traversed vertically by three screws S, S_1, S_2, of $\frac{1}{2}$ mm. pitch, which are placed at the apices of an equilateral triangle of which the axis of the instrument is the centre. They are rounded at their lower ends, are made of hardened steel, and are fitted with nuts W which will screw up and clamp them in any desired position. The screw S is provided with a head graduated into six divisions, and reads against the index-finger I. The pitch of the screw S and the distance between its axis and the line joining the screws S_1, S_2 have been so adjusted that one complete revolution of the screw S will give the instrument a tilt of $\frac{1}{2}°$ about the line S_1, S_2. The graduated head, therefore, reads to 5′ of arc.

The lower end of the plunger P is drilled for the reception of a series of chucks K, on which the crystals are mounted preparatory to being cut. These chucks have been bevelled at various angles ranging at intervals of 10° from 0° to 90°, but in all cases a small surface which is normal to the axis of the instrument has been retained, giving a narrow plane between the cut surfaces. Each chuck has an engraved line on its side which can be brought into coincidence with an index engraved on the side of the plunger, and there clamped by the screw C_1. The ends of the chucks are conical, so that, as the screw C_1 works on an inclined surface, the chuck is drawn up into the plunger, and a good contact between the chuck and the plunger is thus ensured. The zero chuck has its face engraved with a series of parallel lines crossed centrally by a single line at right angles. When the index on the cylinder d stands at 0°, and the lines on the sides of the chucks are coincident with the index on the plunger, the parallel lines on the zero chuck, and the straight edges of the inclined chucks, are parallel to the line joining S_1, S_2.

By the elevation or depression of the screw S, and the consequent tilting of the instrument, the angular value of any of the chucks may be increased or diminished, and thus any intermediate value may be reached.

The principle underlying the application of the instrument is that a crystal mounted on any of the holders may be rotated in two directions at right angles to each other, one of the axes of rotation being that of the plunger P. By means of these two movements it is possible to bring any desired direction in a suitably mounted crystal normal to the grinding surface.

To Set the Axis of the Instrument Normal to the Grinding Surface.—It will at once be seen that in order to cut a plane on a crystal in any definite direction it is necessary to commence operations with the instrument in some position of reference, which may be termed its zero position. This position is attained when the graduated circle around the plunger stands at 0°, bringing the lines and straight edges of the chucks parallel to the line S_1, S_2, and when the vertical axis of the instrument is normal to the grinding surface.

To fulfil the last condition, the usual method employed is that of standing the instrument on an accurately levelled surface, placing a spirit-level on the instrument and turning the screws S, S_1, S_2 until horizontality is obtained. This method, however, is open to serious objections; the small size of the spirit-level used on the instrument does not conduce to accuracy, and it was found, on trial, that some better method must be sought. The method adopted renders the apparatus independent of levels, and at the same time affords adjustments of far greater accuracy.

The instrument is placed on a blackened glass plate. The plunger P is lifted out, and its place is taken by a tube T'_1 of the same diameter, which carries a plate of optically flat glass F at its lower end, set normal to the axis of the tube. The tube is pushed down the instrument until the optical flat is close to the glass plate on which the instrument is standing. The upper end of the tube carries a vertical illuminator T', of the usual pattern, fitted with an inclined cover-glass R.

If light from a signal at a moderate distance away (say 5 feet) be allowed to fall on the cover-glass R, and is reflected down the tube T_1, the observer looking down the tube will see two images of the signal; one reflected from the

surface of the optical flat and the other from the glass plate on which the instrument is standing. By turning the screws S, S_1, S_2 these images may be brought into coincidence, and it is then obvious that the axis of the instrument is normal to the surface on which the ends of the screws are resting. The proximity of the optical flat to the glass plate does away with parallax, for the light forming the two images travels practically the same length of path in each case. This method is sensitive to 2′ of arc.

To Cut and Polish a Plane Surface.—The crystal is mounted on a chuck by means of a thin film of Canada balsam, or of some other convenient medium, and the chuck placed in position in the plunger. In the case of easily cleavable substances it is sometimes found advisable to cover the crystal after mounting with plaster of Paris, to protect the edges while grinding. The instrument is placed on a sheet of plate glass, a small quantity of flour emery[1] or finest carborundum is introduced beneath the crystal, and moistened with a little water. A drop of oil is placed beneath the end of each screw to ensure smooth running. The instrument is held in the hand and moved about on the grinding-plate so that the crystal describes a small circle within the patches of oil in which the screw-legs move. The weight of the plunger is sufficient to keep the crystal in contact with the grinding surface. If carborundum be used, the plane should receive a further grinding on fine emery before it is polished. When a sufficiently large face has been ground, the crystal is cleaned from abrasive material, the screws are wiped free from oil, and the instrument is transferred to a plate of pitch spread with finest washed rouge and water, and moved about as before. A brilliant polish may be obtained by this means on most crystalline substances.

The pitch plate is prepared by pouring well-boiled and strained "British pitch," which can be bought by the pound, inside a brass hoop, 10 inches in diameter, and $\frac{3}{4}$ inch high, which rests on a plane iron plate. The iron plate should not be polished, it should be warm to the hand, and moistened with glycerine to prevent the pitch adhering. When cold, the pitch, with its enclosing ring, may be slid, not lifted, off the iron plate; it will be found to have an excellent lower surface.

For some softer substances, especially calcite, a brilliant polish may be produced by the finest washed putty-powder spread on satin tightly stretched over a plane iron plate, and this method of polishing Nicol prisms is used by some opticians. Others, however, prefer the pitch polisher even for calcite.

As in this instrument we are only cutting and polishing a small central portion of a relatively large area represented by the triangle S, S_1, S_2, the planes so cut and polished are exceptionally flat, and take a polish to their extreme edges.

To Cut a Face Parallel to a given Face.—The instrument being set in its zero position, the crystal is mounted on the given face on the zero holder. It is then ground to a suitable thickness, and polished in the manner described above. Faces so cut are accurately plane and vary very little from true parallelism. The only error introduced is that entailed in setting the given face on the holder, which can be reduced to a minimum by using the thinnest possible film of mounting medium.

Full details of the mode of use of the apparatus for the preparation of surfaces of different orientations, and of the calculations required in the course of these processes, are given in the memoir.

Cutting, Grinding, and Polishing Apparatus of Steeg & Reuter.—This well-known firm of Homburg, so justly celebrated for its preparation of accurately orientated sections of the crystals of naturally occurring minerals, and of those of artificial preparations when of some size, for the study of optic axial interference figures and other crystallographic

[1] Fine emery, taking at least twenty minutes to settle in water.

purposes, constructs excellent crystal-cutting and grinding apparatus, with approximate orientation devices, for work on the larger scale. The following four illustrations show some of their most useful machines.

Fig. 708 represents a grinding and polishing apparatus somewhat akin to Wülfing's. It enables a surface to be ground at any desired inclination to either one or two crystal faces, by means of adjustments with the aid of two graduated circles, and is also of tripod form, with spirit-level. The arrangement will be clear from the figure. The grinding plate is supported on a strong table, provided with levelling screws both for the tripod itself and for the plate. The polishing disc is so arranged that silk, felt, or chamois leather can be stretched over it by means of a ring and tightening screws. The grinding laps supplied with the apparatus are of iron, ground glass, optician's wax, and pewter. Emery of two finenesses for grinding and polishing respectively are also supplied, together with tripoli powder and polishing rouge. A grinding apparatus of the nature of a lapidary's wheel, suitable for larger crystals, is shown in Fig. 709.

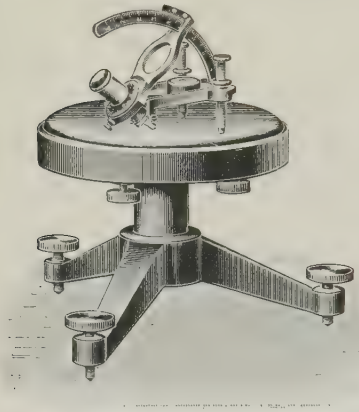


FIG. 708.—Steeg & Reuter's Crystal-grinding Apparatus.

In Figs. 710 and 711 are shown hand and foot machines for both cutting and grinding larger crystals. To either may be fitted a goniometrical orientating and adjusting apparatus for the crystal, although it is actually shown only in Fig. 710 in connection with the vertical hand-driven machine ; it enables the crystals to be rotated and adjusted in three rectangular directions, the three movements being graduated. A further development of the foot machine, Fig. 711, has also been brought out by the firm for motor driving, electric power being now so universal and highly convenient, and is shown in Fig. 712.

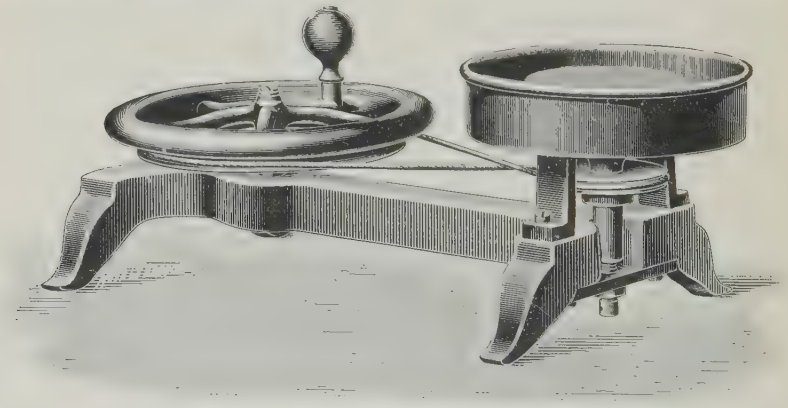


FIG. 709.—Steeg & Reuter's Grinding Apparatus for Large Crystals.

The construction of all these forms of crystal cutting and grinding apparatus will be clear from the figures. The foot and motor-power machines are equally capable of preparing the thin sections of crystalline rocks for microscopic investigation, or the sections or 60°-prisms of mineral or other crystals for more purely crystallographic purposes. Perhaps the instrument for foot driving shown in Fig. 711 combines the greater number of advantages for the latter purposes, with which this book is more particularly concerned. The cutting disc is at *d*, and the grinding lap in a protective well at *m*. The feeding gear, to which the orientating apparatus shown in front in Fig. 710 may be attached instead of the simpler one actually shown, is indicated by the letters *b* and *c*, the latter showing the weighted lever by which the pressure of the crystal against the cutting disc (which must rotate downwards in front) can

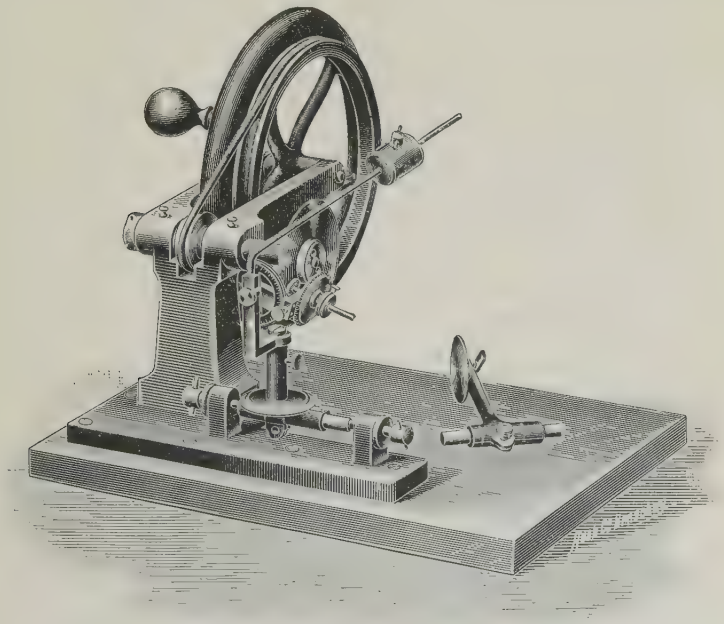


FIG. 710.—Steeg & Reuter's Hand-cutting and Grinding Apparatus with Goniometrical Adjustment.

be modified. A surface is first ground on the crystal, as approximately correct in direction as is attainable by the eye, with the aid of the grinding lap *m*, which should be rotated from left to right, and moist emery. The crystal is then cemented by this surface with shellac on to the disc *a*, both disc and crystal as well as the shellac being warmed to the necessary extent to melt the latter. If the crystal will not withstand this temperature, however, hard balsam in benzene must be used as cement, and then an interval of a day or two allowed to intervene for proper hardening to occur. The disc *a* is subsequently fitted by its perpendicular handle in the crystal-holder, an elbow from *b* or the alternative one of the orientation-fitting shown in Fig. 710, this latter fitting enabling the correct orientation of the crystal to be attained. The feed apparatus to which the crystal-holder is attached is then adjusted for the proper desired thickness of section, the weight *c* arranged to afford a convenient pressure, and cutting proceeded with, the cutting disc being properly fed with moist emery during the process, the receptacle at the bottom of the protecting screen *h* containing

a supply for the purpose, which is applied to the disc from time to time by means of a spoon provided. A set of six cutting discs is provided, three of which are diamond-fed for use with hard crystals, and three for use with emery alone when softer crystals are in hand. The usual varieties of laps are also provided, including one or two of glass, more or less ground. The arrangement shown at *n* is for the gripping of larger crystals or pieces of rock. After cutting off the end of the crystal, leaving the section cemented to the glass plate, the cut surface is ground and polished on *m*, the section removed by warming or dissolving the cement with a solvent, re-cemented by the newly polished second surface, and the first surface then reground and polished truly parallel to the second surface. The section is then finally warmed or dissolved off the disc *a* and mounted on a glass plate or otherwise in whatever manner is most convenient for the purpose in view.

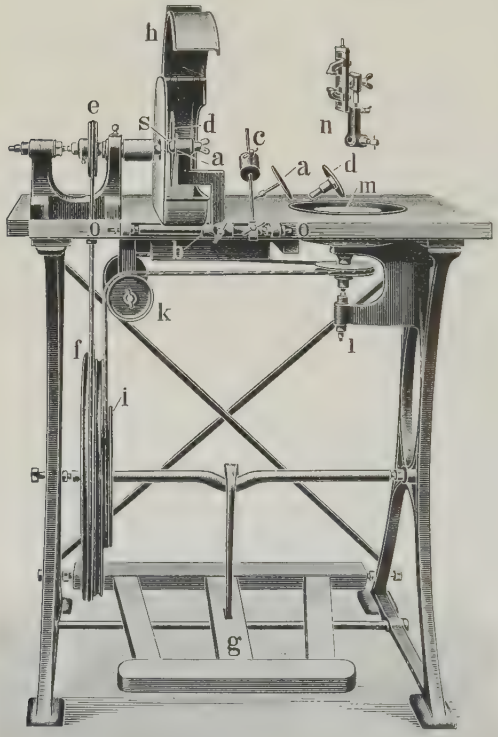


FIG. 711.—Steeg & Reuter's Foot Machine for Crystal Cutting and Grinding.

In the motor-power machine, Fig. 712, the mandril *S* of the cutter, the splash-guard *F*, the grinding lap *T* with its guard *B*, and the apparatus for the support of the crystal *P*, are mutually adjustable with respect to each other. The crystal-holding apparatus *DD'K* shown in the figure is chiefly intended for large crystals or rock pieces, and when smaller crystals are being dealt with it is replaced by the orientating apparatus shown in Fig. 710, which is attached by the two screws *G* to the same feed-apparatus *P*, the details of which are shown in the inset *PP'* beneath the table. The movement is one of sliding of a grooved carrier over four rollers fitting the grooves, the adjustable angle-brackets *V* serving to direct the movement accurately.

The Nature of the Processes of Grinding and Polishing.—A number of interesting facts have been established with regard to what occurs during the processes of grinding and polishing the surfaces of solid substances, of either vitreous or crystalline character.[1]

[1] Lord Rayleigh's Lecture to the Optical Convention of 1905, and two papers by J. W. French, Scientific Adviser to Messrs. Barr & Stroud, *Trans. Opt. Soc.*, 1916 and 1917, give much information.

Glass.—In the case of glass the conchoidal fracture and vitreous-amorphous nature exert a dominating influence in determining the character of the process, rendering it different from the cases of crystals and crystalline metals. A scratch on glass consists of an irregular band of conchoidal cavities of considerable width compared with their depth. Such ordinary scratches on glass, or "cuts" as they are technically termed, are quite different from the "sleeks," or scratches with well-defined edges, which are revealed only in the polished surface (the surface-

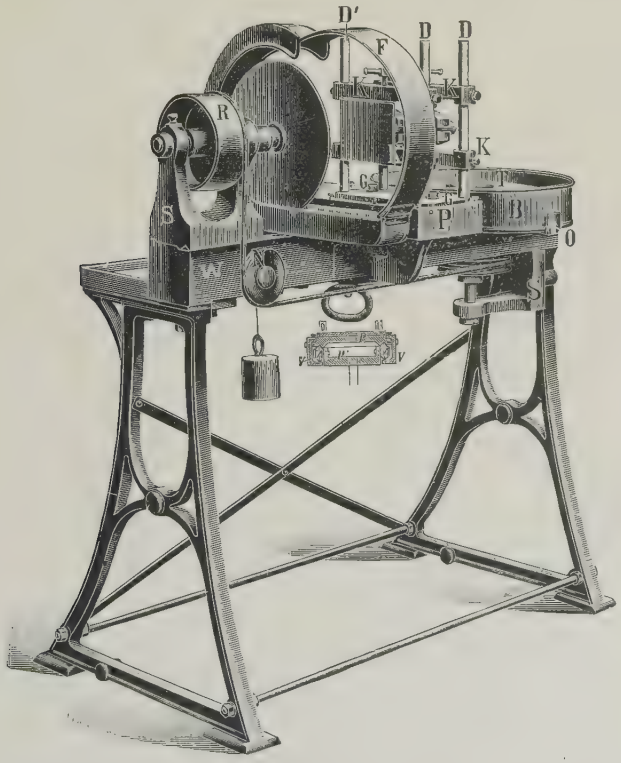


FIG. 712.—Steeg & Reuter's Motor-driven Crystal Cutting and Grinding Machine.

flow-layer, often called β-glass to distinguish it from ordinary or α-glass) of glass by light etching with hydrofluoric acid.

There are three operations in the preparation of glass surfaces, namely, grinding, smoothing, and polishing. In grinding glass, water is used as lubricant, and a succession of abrasives: (*a*) carborundum that has passed through a sieve of 80 meshes to the inch, or coarse emery, or Fontainebleau sand, then (*b*) emery that has passed through 160 meshes per inch, and subsequently (*c*) emery that has not settled in water during forty minutes. The operation *c* may be considered as that of smoothing. For on examining by oblique reflection the surface, smoothed as far as possible with the

finest varieties of the abrasive *c*, some light is generally found to be reflected as if polishing had commenced. It is then surprisingly easy to increase this reflected light and to produce an undoubted polish by the mechanical force of rubbing, say with a piece of wood or even the finger nail, the cohesion of the surface glass molecules being overcome and their re-arrangement in a continuous reflecting surface effected. Something akin to liquefaction occurs, as in the fire-glazing of porcelain by thermal agitation of the molecules. The tool employed in grinding and smoothing is of coarse-grained cast iron, and is either a flat-surface tool or a grinding wheel. Abrasion is quantitatively proportional to the load on the tool and to the speed of its motion.

The tool generally employed for the polishing of glass is a metal plate carrying a flat layer of pitch impregnated with rouge (fine ferric oxide, Fe_2O_3). When this polisher is in use the surface of the glass becomes affected as if by liquefaction, to a depth of 1-4000 to 1-5000th of an inch (about 1-200th millimetre), and the "liquefied" material is removed. The action of the polishing tool disturbs the surface molecules to such an extent as to overcome cohesion, and thus permits their rearrangement as a continuous layer. There should be a change of angle in the motion of the polishing tool every few seconds. As the process of polishing proceeds, more and more glass is removed in this manner, until a perfectly polished surface is produced, by the removal of material below the bottoms of the hollows formed during the earlier smoothing process. Hence the importance of not producing any hollows of unusual depth in that earlier process. A pitch polisher produces a more perfect and optically truer surface than a cloth polisher, because it only touches the tops of the ridges around the hollows, whereas the cloth polisher works and polishes down into them. A polished surface is thus obtained sooner by a cloth polisher, but it is not so truly plane. If we go on with the pitch polisher until all mattness is removed, we get a wonderfully true surface.

There is no evidence of hollows or pits in the original α-glass being filled in or covered over. The investigations of the late Lord Rayleigh are conclusive on this point. He states: "I never saw anything to suggest that pits are filled up and covered over, and my impression is that no material once removed is deposited again, and that the process of polishing has to be continued until all the glass is worn down to the level of the lowest pits." He also considers that polishing is not merely the removal of material, but also a means of producing a surface flow, the two factors combining together to produce the desired effect of a polished transparent surface. There must, however, be a sufficient aim at removal to ensure reaching the bottom of the pits, otherwise some greyness and lack of perfect polish will be apparent.

The β-surface layer has a depth of about eight wave-lengths of red light; this is 8-40,000ths or 1-5000th inch (1-200th millimetre), as above stated. The "sleek" grooves revealed by hydrofluoric acid in the polished surface are about this depth. Optical plate glass, in polishing by hand with rouge and pitch, loses on the average 1-10,000th inch per hour, due to both surface flow and loss of material occurring together. The

finest rouge is composed of particles of the dimensions of two or three red wave-lengths. The rouge may be replaced by manganese dioxide, MnO_2, or by stannic oxide, SnO_2, putty powder, and the former often proves superior to rouge. Polishing a glass surface does not harden it, as in the case of crystals and metals, but slightly softens it.

Hilger has perfected a remarkable method of cementing two optically truly plane glass surfaces, by placing them in optical contact, and then heating them to about 100° C. lower than the softening temperature of the glass. The explanation of this practical fact of glass fusion without apparent softening is, that although the visible portion of the glass, the α-glass, does not soften, the β-layer does actually suffer softening and is deformable at this somewhat lower temperature, and the actual welding occurs between the two β-layers in contact.

Crystals.—The preparation (grinding, smoothing, and polishing) of surfaces on crystals is essentially similar to that described for glass surfaces, with the following important differentiations: that there is no conchoidal fracture as a rule to cause surface cracking, chipping, and flaking; that great care has to be taken with crystals subject to ready cleavage; and that the tools, abrasives, and polishers must be suited to the hardness of the particular crystallised substance. The lubricant also requires to be chosen with reference to the solubility of the crystal substance. With crystals soluble in water, which are usually relatively soft, "brick oil" is used, as already described, and no grinding or polishing powder is used. In some cases, as explained on pages 940 and 943, a trace of moisture (obtained by breathing on the lap) is found to be effective in polishing a slightly soluble substance. As crystals are usually small objects the tool is a revolving lap (a flat disc), as explained in the preceding pages, and its material may be either metal (cast iron, hard white metal, bronze, copper, or pewter) or glass—ground glass for grinding, and polished glass or excessively finely ground glass for polishing. Wood (boxwood being particularly suitable), either alone or faced with broadcloth or chamois leather, and pitch, may also be used for polishing, the particular tool-material being chosen to suit the crystal and its hardness. For the relatively soft crystals of artificial chemically prepared substances the author always uses the glass laps, as described earlier in this chapter. At the one extreme (maximum) of hardness as regards crystals we have the diamond, of hardness 10, which can only be ground and polished with the aid of its own powder and dust, specimens and fragments unsuitable for gemstones being obtainable relatively cheaply and serving as well as perfect specimens for smashing up in a steel mortar. At the other extreme (minimum) of hardness as regards natural crystals we have gypsum (selenite), $CaSO_4 . 2H_2O$, of hardness 2, and the highly important calcite, Iceland spar, $CaCO_3$, of hardness 3, for the polishing of which satin or chamois leather of the softest and finest character, scrupulously free from grit or hard points, has usually to be employed. In the hands of a skilled expert, however, the pitch polisher is capable of excellent results even with calcite, and is preferred for the purpose by one of the best firms of optical instrument makers in this country.

Some very interesting facts have been observed by Sir George Beilby as regards calcite, and described by him in his 1911 lecture to the Institute of Metals, which are worth further notice.

Suitable specimens of calcite cleavage rhombs readily split into plates of uniform thickness, parts of the surfaces of which possess a very perfect natural polish. If a face of this description be gently polished in one direction with a piece of clean chamois leather the surface remains to all appearance unchanged, even under the microscope. But if a drop of very dilute hydrochloric acid be left on the surface for a minute and then washed off, a well-defined pit marks the spot where the acid has rested; this pit has clearly marked edges, and its floor is covered with a multitude of flow-lines or scratches in the direction in which the polishing with the leather had occurred. The soft fibres of the leather under the slight pressure of one finger have penetrated below the surface, and left the tangible records of their passage through the surface layer. The complete obliteration of these records by an apparently undisturbed surface layer is surprising. As the result of step by step etching and careful measurement of the results, it was established that the mechanical disturbance caused by the polishing had penetrated to a depth of 500-1000 $\mu\mu$ (about a thousandth to a two-thousandth of a millimetre), at which depth the disturbance consisted mainly of the deeper furrows. The polishing had so completely flowed the crystal surface, however, that even these furrows had been healed over, so that no trace of them was apparent before the etching. As the surface was approached the furrows of shallower character became fewer, until at a depth of only 100 $\mu\mu$ (one ten-thousandth of a millimetre) furrows of this depth only were practically absent, the flow-lines observed in the polishing of metals being alone revealed by the etching. In the surface layer extending no deeper than 50-100 $\mu\mu$ (one twenty-thousandth to a ten-thousandth of a millimetre) there was no trace of broken-up crystalline material, and the appearance was absolutely homogeneous and vitreous, like a coating of varnish or enamel. Tested with a loaded needle the surface was found to be harder and more tenacious than the original crystal surface. Thus after a surface skin is developed by polishing, it is able to resist the cutting action of powders by which the surface had been satisfactorily ground at an earlier stage. All the evidence points to the fact that liquid-like flow occurs for a depth of 500-1000 $\mu\mu$, and that the substance which results from the solidification of this liquid is in a vitreous amorphous state.

Metals.—As regards the grinding and polishing of metals, the case is more complicated, as we are now dealing not with an individual crystal but with a congeries of crystals, interlacing with one another and situated mutually anyhow with respect to each other; or else the structure is an arrangement of closely packed grains, in each of which the crystals are parallelwise disposed, while adjacent grains are orientated anyhow with respect to each other and to the axes of the crystals which they contain (see Fig. 713, page 956). Indeed most metals as industrially produced consist of such grain aggregates. The crystalline system of the metal is usually either cubic, hexagonal, or trigonal; by exception tin is tetragonal

(ordinary white tin; the rarer form of tin known as grey tin is cubic, as shown on page 694). As in any one grain the crystals lie with their axes parallel, each grain is crystallographically homogeneous. As regards its position with respect to its neighbours, however, with which it is in close contact all over its irregular bounding surface, the arrangement is non-homogeneous, promiscuous, with respect to the crystal axes.

In annealed and cast metals the grains are roughly equal in their directional dimensions, and their external shapes are approximately polyhedral rather than spherical, owing to the contact with their surrounding neighbours. The size of the grains is roughly of the same order, but grain growth can and does occur on heating the metal for a more or less prolonged time, the grains coalescing and the larger absorbing the smaller. The growth appears to occur in the amorphous film which forms the contact surface of a grain with its neighbours, this film re-forming continually out of the smaller grain and handing on its material to the larger, by recrystallisation conformably with the crystals in the larger grain. For instance, Jeffries (as stated in his 1918 lecture to the Institute of Metals) found that a sample of iron, heated to 850° C. for one hour, afterwards exhibited 318 grains per square millimetre. After a similar heating for ten hours there were but 70 grains in this area, and after a week of such heating the whole square millimetre area was occupied by only two and a half grains. The melting point of iron is about 1700° C. absolute, and its lowest recrystallisation temperature is 750° absolute. When a metal is mechanically worked below its annealing temperature the grains are distorted to the extent which is comparable to the distortion of the piece of metal itself, and they are then what is known as "strain-hardened." When a strain-hardened metal is heated above a certain temperature the grains recrystallise normally, that is more or less equiaxed, again. But when the heating is continued just above this recrystallisation temperature the grains grow in size in the manner above described.

It has been shown by D. K. Tchernoff [1] that the mass of a steel ingot is made up of crystallites similar to those found in cavities, and illustrated in Fig. 15 on page 28. When the supply of molten iron is constant, however, the spaces between the axial bars become filled up, the external form of the crystallite disappears, and the whole becomes a grain, which now continues to grow about the same axial directions, as a single crystal of the metal, until arrested by coming into contact with neighbouring similarly formed grains, in which, however, the axial directions are in general different. It is thus that the grain structure of metals comes about. Crystallites first form at the cooling surface of the molten iron or steel (or other metal), whether it be the air surface or the sides of the mould, and they usually grow perpendicularly to the surface into the liquid interior. If cooling be fairly rapid crystallites then begin to form in the interior, at numerous different centres, and eventually produce the crystal grains as just described, and as shown diagrammatically in Fig. 713, their boundaries being produced by the mutual interference of neighbouring grain-crystallites. Each grain is thus an "allotrimorphic"

[1] *Revue Universelle des Mines*, 1880, 7, 129.

crystal, that is, one having an external form determined by the interference of neighbouring crystals.

The crystal-orientation in the different grains is usually revealed by the etching of a polished surface of the metal with an acid; it is also afforded by the polarisation of the light reflected from a polished surface, in the case of metals such as zinc, antimony, and bismuth, which do not crystallise in the cubic system. Zinc crystallises in the holohedral class of the hexagonal system, and antimony and bismuth in the ditrigonal scalenohedral class of the trigonal system.

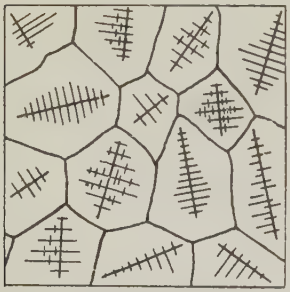


FIG. 713.—The Crystal-grain Structure of Metal.

Uniform growth of crystals from innumerable centres in a mass of molten metal often results in grains being formed of roughly dodecahedral shape. The intergranular bounding surface films, or cell walls, are thin, probably less than ten molecules thick. For Brillouin has found that crystal molecules or polymolecular groups can certainly exert an influence on one another at five molecules distance, and possibly up to eight or ten molecular distances; so that the crystals cease to grow when they reach this proximity to each other, leaving intervening connecting films of the metal still uncrystallised. It is probably these films or cell-walls which enable the grains to move about each other, when the metal is subject to mechanical working at different temperatures.

It is a curious fact that metals grown from the molten state very rarely form single individual crystals with perfect exterior form, exhibiting the crystal faces characteristic of the system and class of symmetry. They vastly prefer to produce the skeletal, arborescent, or other dentritic crystallite-forms, probably because they begin to crystallise in the labile condition of superfusion. Good crystals for crystallographic investigation are, therefore, very difficult to obtain in the case of metals, and they have generally to be specially prepared by sublimation *in vacuo*, or by slow electrolytic deposition under specially favourable circumstances.

It is necessary that these interesting facts about metals should be appreciated, in order that the processes of the grinding and polishing of metals may be rightly understood. The machines shown in Figs. 711 and 712, with grinding lap in a sunken well, are very suitable for the grinding and polishing of sections for metallographic photo-micrographic purposes, using the abrasive already mentioned. The polishing materials used are rouge, the finest alumina, stannic oxide, and chromium oxide, and the lap may be covered first with the finest emery cloth and subsequently with carefully selected chamois leather or "selvyt" cloth, stretched tightly over the lap by means of the usual encircling hoop and binding screws.

When the surface of a piece of metal is scratched, as by the tool in turning on the lathe or in grinding with emery or other abrasives, each

scratch consists of a groove which is deep compared with its width. It is the result of the tearing away of masses of crystals or crystal grains, and also of the "swaging" of the material. When such a scratched metallic surface is polished with the burnisher, or with rouge or any of the other polishing powders mentioned, the grooves become covered over with a continuous surface or "flow-layer," and disappear. If the surface be removed by acid etching the grooves reappear. According to Sir George Beilby (*loc. cit.*) the cohesion of the surface flow-layer is so considerable that comparatively large areas can be thus bridged over, without the groove becoming first filled up with any supporting debris. The force exercised in the rubbing of the surface by the polisher overcomes the cohesive and crystallographic forces, which normally bind the molecules together, and produces a continuous reflecting surface by the uniform rearrangement of the molecules in the surface skin, with the aid of the surface tension forces. The irregularities in this highly reflective polished surface are often less than a wave-length of red light, thus essentially differing from those of the original surface before the polishing, which were very great compared with a wave-length of light and therefore caused scattering of the light.

An interesting account of experiments on "Crystal Growth and Recrystallisation in Metals," by Prof. H. C. H. Carpenter and Miss C. F. Elam, was communicated to the Institute of Metals at their Autumn Meeting at Barrow-in-Furness, 1920, and is published in *Nature* of Nov. 4, 1920, vol. cvi. p. 312. They indicate the importance of distinguishing clearly between "crystal growth" and "recrystallisation," the latter meaning complete re-orientation of a crystal or a group of crystals, starting from new centres, while the former refers only to a rearrangement by which certain crystals increase in size at the expense of the material of others. They show that cutting, filing, and even grinding on the finer emery papers often bring about spontaneous recrystallisation of the surface layer of a metal, which can only be removed by polishing and etching. With an alloy of tin with 1·5 per cent. of antimony they have been able to study experimentally the stages of crystal growth. By alternately immersing the specimen in ammonium sulphide solution, and rubbing it on selvyt or chamois leather with magnesia moistened with ammonium sulphide, a very beautiful surface was obtained, the separate crystals or crystal grains being clearly demarcated, and the various stages of the growth of crystal grains after heating to 150-200° C. for definite intervals of time were indicated by clear boundary lines. It was also possible to distinguish between the crystal growing and the crystal being grown into. They have established (1) that crystal growth always takes place by gradual boundary migration and not by coalescence; (2) growth may occur either of a large crystal into a small one, or of a small into a large one; (3) a crystal which is itself being invaded by one crystal may simultaneously grow at the expense of another; (4) the rate of growth is not constant for any given time at a particular temperature; (5) all available evidence indicates that the crystals of castings do not grow after their first formation; (6) the largest crystals are formed by annealing

at a relatively high temperature ; (7) growth and recrystallisation can be induced by work. The true cause of crystal growth, and of recrystallisation followed by crystal growth, is finally considered to be plastic deformation followed by heat. As regards the viscosity of metals, the salient facts are given on page 554.

The subject of the crystallisation of metals has given rise to much discussion and some controversy. The controversial questions, however, may be left for further experimental work to decide. What has been stated in the foregoing account represents the facts which have definitely been settled by direct experiment.

CHAPTER XLIV

THE PRODUCTION OF MONOCHROMATIC LIGHT

THE most satisfactory source of monochromatic light for practical crystallographic purposes is the continuous spectrum itself, filtered through a selecting slit, of fine opening, which permits a band of not more than a two-hundredth part, and preferably only a three-hundredth part, of the visible spectrum to escape. It should be produced from a powerful origin, best of all from the electric arc, by means of a single refracting prism, a grating affording insufficient light. The two refracting surfaces of the prism should be truly plane, and the prism itself of highly refractive and dispersive glass, but perfectly colourless so as to transmit the violet end of the spectrum without absorption. The objectives and optical tubes should also be of wide aperture, in order to transmit as much light as possible, which permits of the desirable narrowing of the exit slit.

A form of apparatus which admirably fulfils these conditions has been in use by the author since the year 1893, and was described to the Royal Society in February 1894.[1] It is shown in Fig. 714, and also in Fig. 715 in actual use with the electric lantern as source of light, to illuminate the polariscopical goniometer in a determination of the optic axial angle of a crystal.

It is essentially a very compact spectroscope, constructed to transmit as much light as possible. The two optical tubes *a* and *b* (see Fig. 715 for letters) are exactly alike, each carrying an adjustable slit *c* at one end and an achromatic lens *d* of nine inches focal length and two inches diameter at the other, the former being carried in an inner draw-tube so that the slit may be accurately adjusted to the focus of the objective by means of a rack and pinion *e* which effects the movement of the draw-tube. The pair of lenses forming each objective are separated by an air-film or narrow cell, in order to minimise the passage of heat rays. Either optical tube may be used as telescope and the other as collimator. That which is chosen as collimator (*a* in Fig. 715) is complete as already described. The other *b* chosen for use as the telescope is at once converted into such by screwing on to a tapped annulus, which is carried by both tubes in front of the slit, a cap *f* (lying on the base in Fig. 715) carrying a short tube in which slides an eyepiece. Three interchangeable eyepieces are provided (the two others being *g* and *h*), magnifying respectively two (*g*), four (*f*), and six (*h*) diameters. When one of the optical tubes is left in its simple condition, and the other is fitted with one of these

[1] *Phil. Trans.*, 1895, A, *185*, 913.

eyepieces, the two tubes are precisely those of an ordinary, although very compact and stout-tubed, spectroscope. The instrument is, in fact, used as such—with its collimator slit nearly closed but the telescope slit in front of the eyepiece opened wide, serving merely as a diaphragm aperture—for observing the Fraunhofer lines and employing them (with the telescope slit narrowed down again) for the purpose of the calibration of the instrument for the delivery of light of a number of definite wave-lengths, or for the observation of the bright lines of sodium, lithium, thallium, hydrogen, mercury, cadmium, neon, or helium, for the like purpose. The two optical tubes are carried in a similar manner on counterpoised arms *i*, adjustable and capable of fixation by milled-headed clamping screws *j* at any relative positions about the circle *k*.

The prism *l* employed on this instrument is a large one of 60° angle in order to receive all the light emanating from the objective of the collimator, the refracting

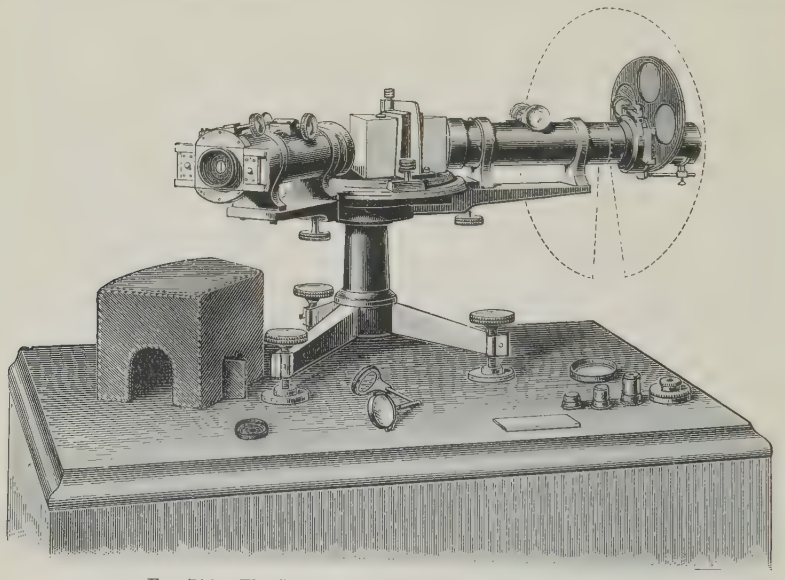


FIG. 714.—The Spectroscopic Monochromatic Illuminator.

faces being $4\frac{1}{2}$ by $2\frac{1}{2}$ inches. This fine prism has also the exceptional double advantage of affording unusually large dispersion, nearly twice that of ordinary flint glass, while being perfectly colourless and unabsorptive. A Hilger constant-deviation prism may be used instead, however, although experience shows that it does not transmit as much light as the author's prism, nor does it yield as much dispersion; also, it is not so free from colour and absorptive effect. It is, however, a very convenient form of prism, the deflection being uniformly 90°, and for most purposes it serves quite well. When a Hilger drum calibrated directly in wave-lengths is used in connection with it the arrangement, shown later in this chapter in Fig. 716, is particularly convenient. As Messrs. Chance have hitherto been unable quite to reproduce the glass of the author's prism, a Hilger constant-deviation prism, with calibration drum, may be recommended as the next best substitute, and the instrument as thus constructed is now furnished by Hilger. The glass from which the author's prism was cut was one-half of a block prepared by Messrs. Chance for the late Sir William Huggins, for the purpose of a prism for his star-spectroscope, the desiderata being the same as for the author's spectroscopic illuminator. By the kindness of Sir William Huggins, there being ample

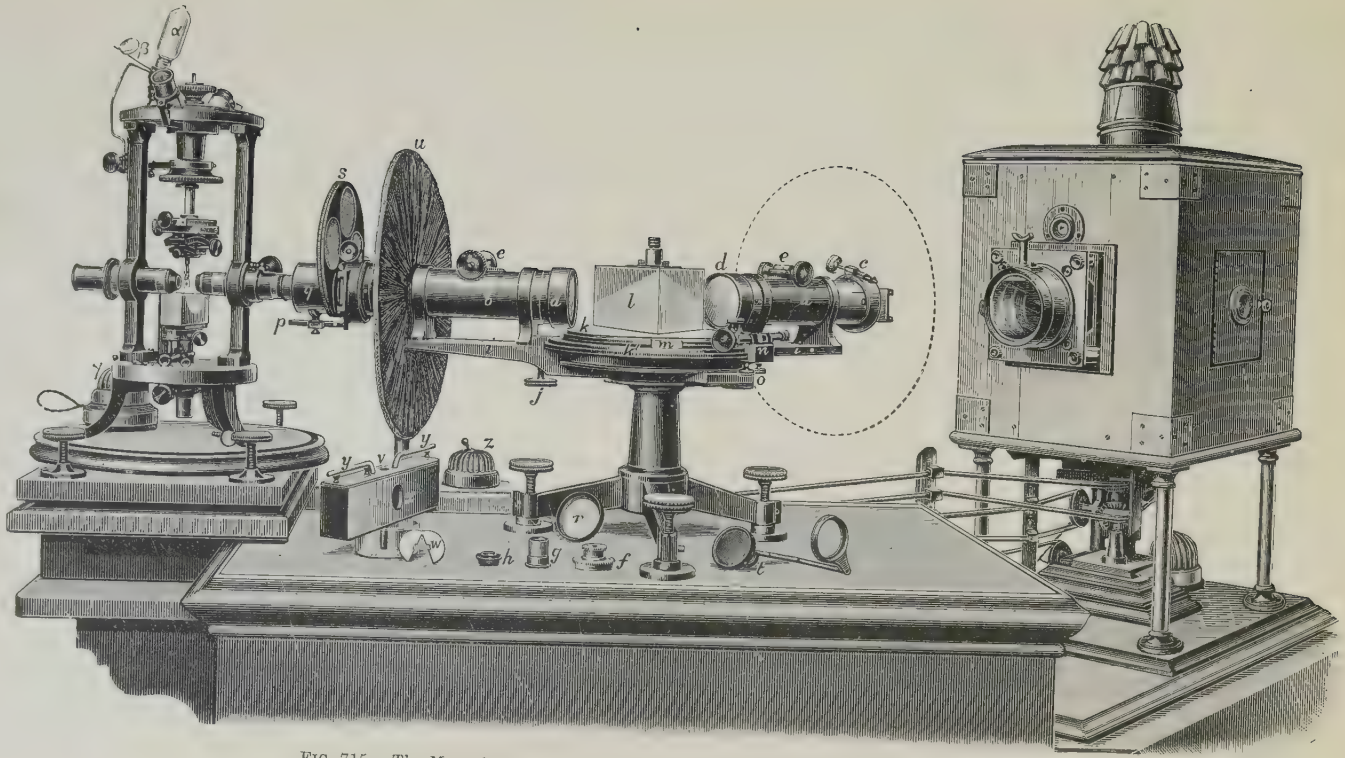


FIG. 715.—The Monochromatic Illuminator in Use with the Optic Axial Angle Goniometer.

glass for two large prisms, the author's prism was cut from one half, and the star-spectroscope prism from the other half.

The prism l is mounted on a rotating divided circle k, reading directly to half-degrees, and to single minutes with the aid of the vernier m attached to the fixed table k'. It is provided with a fine adjustment n extending for 7°, which is just ample to enable the whole spectrum to be traversed past the exit slit (that of the tube used as telescope, the eyepiece being removed and the slit closed down to the same fine opening as that of the collimator). When the Hilger drum is employed, it simply replaces this fine adjustment, which is readily detachable, the screw and spring-piston portion being attached to the fixed circular plate k', and the projection moved by the screw and held between it and the piston being part of an attachment to the circle k, both attachments being by a pair of milled-headed screws, o in the case of the lower one, the vernier plate or circle in each case being gripped by a bracket through which the screws pass.

When in use for the purpose of producing monochromatic light the eyepiece and its screw-cap attachment are removed from the telescope, and replaced by an annulus bearing a similar screw thread and carrying at right angles a horizontal rod p of square section, over which fits a little slider carrying above a wide but very short tube q in which in turn slides the carrying frame of a ground-glass plate. Two such interchangeable plates are provided of different finenesses of ground surface, ready mounted in their own annular carrier-frames ; one is shown resting on the base against the tripod at r. The finer is preferable for use when refractive indices are being determined, and the coarser when optic axial angles are being measured. The use of this ground-glass screen is to diffuse slightly the linear beam of monochromatic light streaming through the exit slit, the beam being the narrower the finer the slit and more perfect the monochromatism. After such diffusion the light is capable of evenly filling the field of any optical instrument, such as a refractometer or polariscope, which is brought in front of the ground-glass screen, when the slit of the collimator is illuminated by the converging beam of brilliant light from the condenser of the electric lantern.

It is found with such an arrangement—the two optical tubes being fixed at the suitable angle found by experiment, and the prism free to rotate—that there is a particular angle of setting of the two optical tubes with respect to each other and the prism, near but not quite that for minimum deviation for any ray of the visible spectrum (a wave-length in the ultra-violet being really set for minimum deviation), at which, by rotation of the prism, the whole of the visible spectrum may be caused to pass the exit slit of the second optical tube. Both optical tubes are clamped when this position is found, and remain always afterwards fixed. The prism is also clamped to the circle by means of the milled-headed screw working through the top of a bracket fixed to the circle plate, most of the pressure being taken up by a three-armed convex plate lying on the prism to protect it from the screw. If the Hilger constant deviation prism be used, the optical tubes are fixed at 90° once for all.

Any stray white light, or coloured light of other than the desired wave-length, due to internal reflections from the glass or inner tube surfaces, may be cut off completely by introducing a screen of either ruby-red, signal-green, or cobalt glass, or a combination of these two latter glasses, between the exit slit and the ground-glass screen. A couple of rotatable discs s, each furnished with four circular windows arranged like a quatrefoil, three of which contain these coloured glasses while the fourth in each case is left an open aperture, are supported in a dovetailed fitting above the slit box ; the bevelled bracket carrying the axle on which the discs rotate and which slides in the dovetail is so arranged that when pushed home the discs are suspended so that any window may be brought by rotation of the disc exactly in front of the slit, with the centre of the window in the optical axis. The two discs are each separately rotatable about their common axis carried by the bracket. Hence, either the two blank windows

can be brought opposite to the slit, when the monochromatic light streaming from the latter goes through unaffected, or any one glass window, or any combination of two differently coloured glass windows, may be arranged in the path of the emerging rays, and be thus used as light filters. This accessory proves very useful in the case of the investigation of crystals showing great change of optic axial angle with different wave-length of the illuminating light; for the presence of stray white light blurs the sharpness of the interference figures, and in extreme cases destroys the figures altogether or renders them useless for measurement purposes. The accessory is not required for the middle part of the spectrum about the yellow, nor is it at all necessary when the instrument is being used as illuminator of the spectrometer-goniometer during the determination of refractive indices.

On the base-board of the instrument as seen in Figs. 714 and 715, several accessories are shown, besides the eyepieces and the second ground-glass screen already alluded to. One is an adjustable mirror (*t* in Fig. 715), carried by an annulus gearing with the screw thread on the tapped circular rim in front of the slit of either optical tube. This enables sunlight to be directed on the entrance slit when desired, from a heliostat or otherwise. There is also a velvet-covered shade (shown in Fig. 714) for the prism and the objective ends of the optical tubes, which enables the apparatus to be used in daylight as well as in a darkened room. A circular screen is also shown at *u* in Fig. 715 and indicated in dotted lines in Fig. 714, near the exit end of the second optical tube. This is a wire fitting covered with radial folds of dark green silk cloth, and serves to screen off any stray lantern rays from the observer's eye. A similar screen is usually also fitted near the entrance slit end of the first optical tube, as indicated by the dotted ellipse in Fig. 715, in order to prevent such rays getting directly at the prism or second objective. Another little accessory shown on the base in Fig. 714 is an elongated, rectangular, bevelled-edged, ground-glass plate, the same size as the jaws of the slit. Its purpose is to act as a screen for the reception and direct inspection of the spectrum, the slit-jaws being removable by unfastening a simple locking device and sliding them out, when the bevelled glass slip can be pushed into the dovetailed recess, thus left, instead.

Calibration of the Instrument for the Exit of Monochromatic Light of Specific Wave-lengths.—To calibrate this illuminator so as to know what divisions of the circle correspond to the issue of light of known wave-lengths, the entrance slit is illuminated by sunlight reflected from the mirror fitting, the slit being closed down to a very fine line by means of the adjusting screw, which moves each jaw independently and oppositely, so as to maintain the centre of the slit constant. The middle power eyepiece *f* is fitted to the other optical tube instead of the ground-glass diffuser, and the Fraunhofer lines examined as in an ordinary spectroscope, at first with the exit slit opened wide to reveal a considerable portion of the spectrum, but subsequently closed down for the placing of any Fraunhofer line to its centre.

The opening of the exit slit may be so narrow that when focussed by the eyepiece the two jaw edges appear only slightly further apart than is necessary to permit the two sodium D-lines to be seen between them, the jaws serving as a couple of spider-lines; the D-lines (or any other line adjusted) appear parallel and symmetrically placed between them. If the optical tubes have not yet been fixed in their proper positions, they are arranged at first in the usual well-known way for minimum deviation of the middle part of the spectrum. The jaws of the exit slit may be removed altogether if desired, so as to obtain a full aperture during this review of the spectrum, for the locking device referred to enables removal to be accomplished without deranging their adjustment when replaced again. Moreover, even if not removed, as the fine adjustment of the slit is arranged to move both jaws equally, any spectrum line adjusted between them remains approximately so when their opening is varied, even to the extent of full aperture.

The telescope is then moved so as to pass through the spectrum from red to blue

and as far as a position at which the last traces of visible spectrum have just disappeared; it is then fixed there and the collimator likewise fixed, a wave-length in the ultra-violet being thus set for minimum deviation. On rotation of the prism and its circle in either direction the whole of the colours of the spectrum in succession will move past the vertical diameter of the field. That one of the two directions is then chosen, for which the greater loss of light by reflection from the receiving surface of the prism occurs for the red end, as the illuminating powers of the different parts of the spectrum are then more nearly equalised. The entrance slit being set to a very fine opening as above mentioned, the definition of the Fraunhofer lines is still excellent when focussed by the rack and pinion of the telescope. The fine adjustment for the divided circle is then set so as completely to carry out this movement of the whole spectrum, about 7°, past the centre of the field.

The exit slit-jaws are next replaced, or if they had been simply opened wide they are closed up to the fine opening already specified, through which when the prism circle is rotated to the right position the two solar D-lines may both just be seen clearly focussed between the two jaw-edges. The reading of the circle is then recorded. This reading should afterwards be confirmed for the bright sodium lines by means of a sodium flame. The prism circle should then be rotated and other prominent solar lines adjusted and their circle readings recorded. The readings for the red, greenish-blue, and violet hydrogen lines Hα, Hβ, and Hγ, at C, F, and near G of the solar spectrum will be included among these, and they should next be confirmed by means of the bright lines afforded by a hydrogen Geissler tube. It is advisable also to determine the readings for the red, green, and blue lines of cadmium and for the green line of mercury, with the aid of Geissler tubes or the cadmium-vapour arc lamp or mercury-vapour lamp (see pages 971-973), as these rays are now much used in optical work. Similar readings should also be taken for the red lithium line and the green thallium line, when flames coloured by the salts of these two metals are produced just as for sodium light. Moreover, from time to time it is well to check the readings of the circle for the issue of the three metallic lines from the centre of the exit slit, certainly always before any original investigation is undertaken. For this purpose the author has always at hand a mahogany box (shown to the left in Fig. 634, page 855), lined and pyramidally terminated above (as a chimney) with tinned iron, and furnished with a large glass window which can be placed opposite the entrance slit of the illuminator, with a door at the back, and with a perforated base raised a couple of inches so as to admit air freely beneath. A Bunsen lamp is placed within, the gas-tube connection being passed through one of the basal perforations, and a set of three stout platinum wires terminated by platinum boats are arranged at the height of the flame on a brass standard which is rotatable from without by means of a lever handle projecting from under the raised base; so that when the three salts are placed in the boats any one of the latter can be rotated into contact with the flame, and thus all three metallic lines can be rapidly reviewed and their situations verified by rotating the prism to the graduations corresponding to them.

If on thus reviewing each of the three lines it should not prove to be quite central between the jaw-edges of the exit slit, as focussed simultaneously with the lines by the eyepiece, the prism circle should be adjusted until it is, and the exact reading noted. As the jaws of the slit have occasionally to be opened a little wider when very small or imperfectly transparent crystals are under investigation, and then subsequently nearly closed again for use with good crystals, these variations, although the jaws are arranged to move equally on each side of the centre, may cause minute differences of circle readings to occur, which require to be observed. Such differences, however, have never been found to exceed 2′, and the minute correction is the same for all the lines. In the case of the sodium D-lines, even the lowest power eyepiece separates them, and the middle power which is generally used shows them an apparent

millimetre apart. The reading for sodium light is taken when they are symmetrically placed between the two slit-jaws, the separation of which is about double that of the two lines.

In order that the readings for all wave-lengths may be known, and the prism-circle set for any wave-length at any time, the results of the calibrations are graphically expressed on curve-paper, taking circle readings for ordinates and wave-lengths for abscissæ; the curve joining the points on it thus graphically set forth is then drawn with a free hand. It is subsequently only necessary, in order to procure light of any wave-length whatsoever, to set the circle to the reading indicated by the curve as corresponding to this wave-length, and to illuminate the entrance slit with the powerful white light from the lantern, when monochromatic light of the desired wave-length will stream through the exit slit, and, the eyepiece in front of it being removed and the ground-glass diffuser added instead, will form a brilliant patch on the diffusing screen, adequate to illuminate any observing instrument.

If the Hilger constant-deviation prism and wave-length drum are employed, the actual wave-lengths themselves of the various spectrum lines adjusted between the slit-jaws are marked on the drum directly. The calibration in this case is very conveniently done with the aid of the arc spectrum of copper, the copper lines affording an adequate number of fixed wave-lengths in themselves to enable most others to be obtained by interpolation, and they can always afterwards be verified as regards the sodium, lithium, and thallium lines. Messrs. Hilger generally supply the drum as thus calibrated by means of a copper arc.

This monochromatic illuminator is especially useful when some exceptionally interesting phenomenon is observed—the crossing of the optic axial planes and production of a temporary uniaxial figure by a biaxial crystal for instance—with light of a wave-length intermediate between the wave-lengths corresponding to two spectrum lines, say somewhere in the green between sodium and thallium light, and for which it is desired to know the exact wave-length. It is only necessary to take the circle reading when the particular phenomenon (say the uniaxial figure) is produced, and consult the curve, or if the Hilger drum is in use to take its indication, in order at once to ascertain the required wave-length.

The author's instrument was constructed by Messrs. Troughton & Simms, and has proved most efficient, having the great advantage of the exceptional dispersion of its magnificent 60°-prism. Similar instruments have been supplied to the Mineral Department of the British Museum and to the Manchester School of Technology, which are almost equally effective, although the dispersion is not quite so great, on account of the difficulty in reproducing the original glass.

The Hilger Wave-length Spectroscope adapted as Monochromatic Apparatus.—As already mentioned, the author's 60°-prism and circle fine adjustment may be replaced by a Hilger constant-deviation prism and wave-length drum. As many ordinary spectroscopes have now been supplied by Messrs. Hilger fitted with these arrangements, it may be useful to state that they can at once be adapted for the production of

monochromatic light by simply replacing the two optical tubes by a pair with the author's special fittings, and which are shorter and stouter in order to afford a wider objective aperture and to transmit a great deal more light. The objectives are 31·5 mm. clear aperture, and their focal length only 185 mm. Such an instrument, constructed by the firm of Hilger under the author's supervision, is shown in Fig. 716. The wave-length drum is also shown enlarged in Fig. 717 and a plan of the constant-deviation prism, showing the path of the light rays, in Fig. 718. The indication of the wave-length on the drum is made by an indicator projecting from the fixed frame and which bears a narrow rib

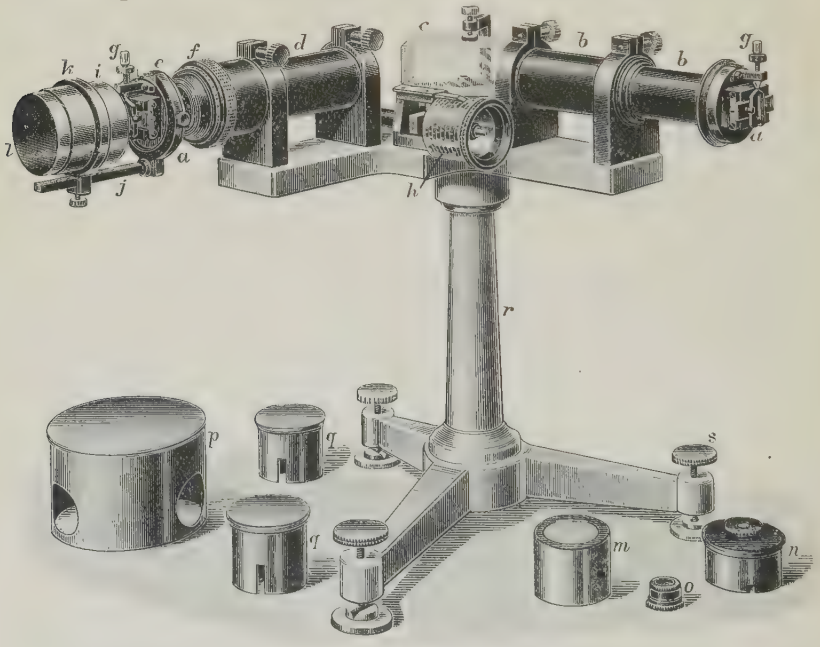


FIG. 716.—The Monochromatic Illuminator with Constant-deviation Prism and Wave-length Drum as constructed by Hilger.

below, gearing in a helical slot in the cylindrical surface of the drum. The prism is of the Pellin-Broca type, the shape of which will be clear from Fig. 718. It may be considered as built up of a couple of 30°-prisms and a right-angled totally-reflecting prism, and it is from the hypotenuse of the latter that the internal reflection occurs. The path of the rays is indicated by the thick dotted line and the arrows, I being the incident ray and R the finally refracted ray. As the light rays pass through the 30°-prisms at right angles to one of the imaginary planes (the internal one) forming the 30°-angle in each case, and parallel to the imaginary or real base which is perpendicular to that plane, the refracting effect is as if the rays had traversed a 60°-prism parallel to the base, that is, at minimum deviation, but as one of the 30°-prisms is inverted

relatively to the other, the deviation produced by that other is neutralised; then between the two the reflecting prism reflects the ray rectangularly, and thus the refracted ray finally emerges making an angle of 90° with the incident ray. Moreover, the deviation remains constant at 90° for all wave-lengths, rotation of the prism[1] by the wave-length drum simply bringing successive colours thus deviated past the centre of the field, the telescope and collimator being fixed at right angles to each other This instrument has been thoroughly tested by the author, and proves very efficient. Although the intensity of the monochromatic light afforded by it is not quite as great as that delivered by the Troughton & Simms instrument, the purity of the spectrum is greater, and it is quite unnecessary to employ the coloured-glass filters. The two slits *a* are of identical construction, the jaws moving equally, on each side of their closed position, when manipulated by the adjusting screw *g*, seen above the slit. It is convenient to employ the optical tube *b* seen to the right in Fig. 716 to receive on its slit the converged beam of light from the lantern, as the wave-length drum *h* can then be more readily manipulated by the right hand than when the other tube is so used. After preliminary adjustment of each slit to the focus of its respective objective, the final focussing of the spectrum to the exact plane of the exit slit (the spectrum lines being then focussed by the eyepiece simultaneously with the jaws of the exit slit) is best performed entirely on the second optical tube *d* carrying the exit slit and eyepiece; it is achieved by means of a milled rotatable focussing ring *f*, which acts as a driving nut replacing the ordinary rack and pinion and affords a very steady fine adjustment. The eyepiece is carried in a detachable cap *n*, seen lying on the table to the right, which slips on to the exit slit end of the optical tube when required for observation or calibration of the spectrum lines; two interchangeable eyepieces are supplied (the second being shown at *o*), adjustable in the cap so as to focus the slit, the one clearly dividing the two sodium lines

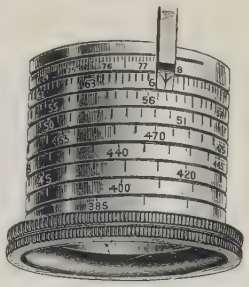


FIG. 717.—Hilger Wave-length Drum.

[1] According to W. E. Forsythe (*Astro. Phys. Journ.*, 1917, *45*, 278) the proper point of rotation of the prism is the intersection of the bisector of the angle between the incident face and the base (the long lower left face in Fig. 718) with the reflecting surface of the prism. When the prism is rotated about this point there is no lateral shifting of the beam, and the calibration will not depend on the character of the spectroscope lenses. The same conclusion was independently arrived at by E. Bloch (*Journ. de Physique*, 1917, *7*, 145), who showed that if A be the top 75° corner of the prism (Fig. 718), and P be the invariable point or centre of rotation in question —such that if the prism be rotated about an axis passing through it perpendicularly to the plane of the paper in Fig. 718 (the position of the incident ray remaining fixed) the emergent ray also remains fixed in position—then the position of this point P on the reflecting (upper right) face is afforded by the equation:

$$\mathrm{AP} = \frac{a \sin 45^\circ}{\sin (75^\circ + 45^\circ)} = \frac{a \sin 45^\circ}{\cos 30^\circ} = 0{\cdot}816a,$$

where *a* is the length of the incident (upper left) face.

and the other separating them to the extent of an apparent millimetre. When the exit slit is opened wide and the eyepiece is in position the instrument is a most efficient wave-length spectroscope.

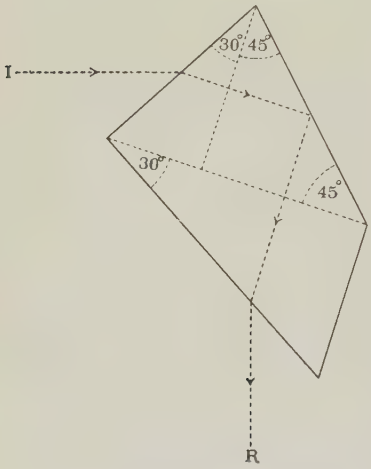


FIG. 718.—Construction of Constant-deviation Prism.

Ordinarily, when the instrument is in use as a monochromatic illuminator, the eyepiece is replaced by the diffusing-tube fitting *i*, capable of sliding along a bar *j* by means of a collar *k* carrying below a slider; the bar is carried by an annulus *e* attachable by two milled-headed screws. The short sliding tube is provided with two alternative movable inner tubes *l* and *m* (the latter shown lying on the table next to the eyepiece) each carrying a ground-glass screen, one being more finely ground for refractive index determinations and the other coarser for optic axial angle observations. The constant-deviation prism *c* is provided with a metallic cover *p*, pierced with two apertures opposite the objectives of the optical tubes. It is shown resting on the table to the left. The other two objects on the table are a pair of cover-caps *q* to protect the slits when the instrument is not in use. The whole instrument is mounted on a stout pedestal *r*, and tripod provided with levelling screws *s*.

Subsequent to a visit paid to the author in Oxford by Prof. Wülfing, when the monochromatic illuminator was seen at work as shown in Fig. 715, an instrument termed the "Wülfing" monochromatic illuminator has also been constructed and catalogued on these lines by Fuess of Berlin, and is shown in Fig. 719. In this instrument, which also includes a constant deviation prism and wave-length drum, the author's ground-glass diffuser is replaced by a lens, on the recommendation of Prof. Wülfing. The author's earlier experiments with lens diffusers, however, led him to discard them for the ground-glass diffuser, which is infinitely more satisfactory provided a brilliant source of light, the electric arc, is available.

Geissler Vacuum Tubes, Mercury-Vapour and Cadmium-Vapour Lamps.—The most suitable form of Geissler vacuum tube for all the purposes referred to in this chapter and in the later chapters L., LVII., and LVIII., concerned with polarimetry and interferometry, is of H shape, as shown especially clearly on the right in Fig. 890, Chapter LVII., and in Fig. 897 in Chapter LVIII. Excellent tubes of this type are made in this country by Mr. Cossor, and are also supplied by Messrs. Hilger. The highly-rarefied gases found most useful are hydrogen, neon, and helium, mercury vapour (derived from an enclosed globule of mercury), and cadmium vapour. The wave-lengths of the principal spectrum bright lines, the light of which it is desired to use, are given in the table

on page 798. In the case of the cadmium-vapour lamp the H-tube encloses a small pellet of metallic cadmium, and to render it effective the tube requires to be heated to 200° C. in order to volatilise the metal. A small enclosing air-bath fitted with thermometer and heated by a small Bunsen burner is the safest arrangement for heating it. There are two modes of actuating vacuum tubes, by the Ruhmkorff induction coil, or by a transformer furnishing a high-tension alternating current. If the Ruhmkorff coil be employed, the proper current can readily be obtained by passing the 100-volt direct (continuous) supply current through 4-6 32-candle-power carbon-filament lamps arranged "in parallel." The author has a covered metal box for the purpose, fitted with lamp socket connections for 8 such lamps; only those lamps as are required are placed in position in their sockets. Each permits about $1\frac{1}{2}$ ampères of

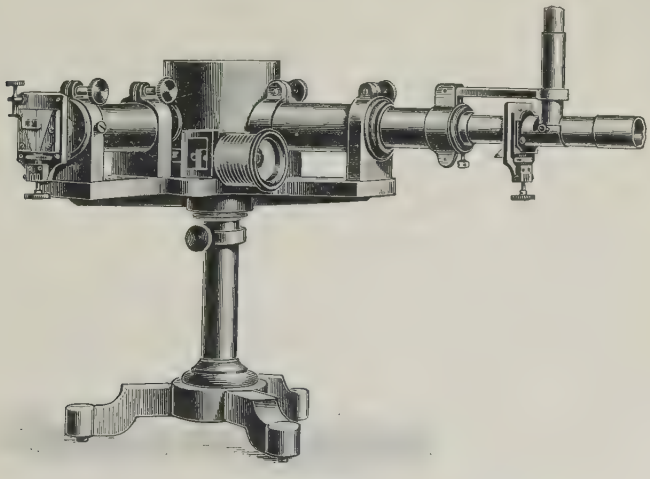


FIG. 719.—Fuess-Wülfing Monochromatic Illuminator.

current to pass to the primary of the coil, a total of 6 ampères from 4 of the lamps being usually suitable. The author's coil is a large one capable of affording a six-inch spark between the adjustable sparking terminals of the secondary.

A high-voltage transformer and converter outfit is supplied by Messrs. Hilger specially for vacuum tube work. It consists of a $\frac{1}{4}$ kilowatt rotary converter taking 110 or 220 volts direct current and converting it into a 75 or 150 volts alternating one, shown on the left in Fig. 720, and a $\frac{1}{4}$ kilowatt transformer (seen more to the right of the figure) giving approximately 15,000 volts with 150 volts on the primary, and a 50-candle-power carbon filament lamp (two being provided) inserted "in series" with the primary of the transformer. When an alternating current is available the converter is not required, and the transformer can be run direct off the mains, its use being to transform the low voltage of the primary (that of the supply current, 150 volts, say) into a high voltage in the secondary; it acts, in

fact, like a Ruhmkorff coil, but the supply must be alternating, whereas the primary of the Ruhmkorff coil requires to be supplied with direct current. If a condenser (seen in the centre of the figure) be added ($\frac{1}{4}$ kilowatt) the outfit can also be used for sparking between electrodes, the condenser being connected in parallel with the secondary of the transformer.

As regards hydrogen vacuum tubes, the primary spectrum, which is

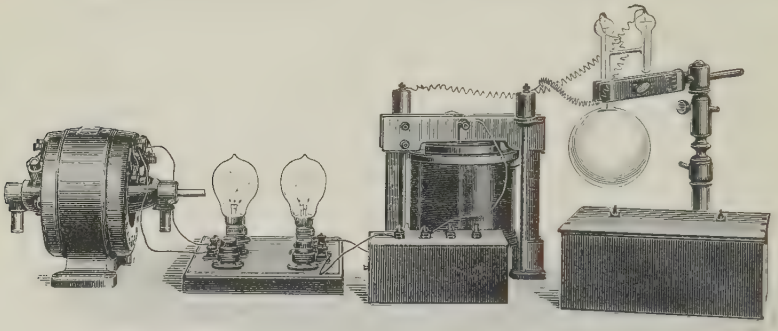


FIG. 720.—Converter and Transformer for Vacuum Tube Work.

what is needed and is indicated by the bright red glow in the capillary cross-tube of the H, usually deteriorates more or less rapidly with use, owing to the impairment of the vacuum by the liberation of hydrogen occluded in the electrodes, the secondary spectrum being afforded instead at the higher pressure. This can be largely counteracted by blowing a large bulb on one of the limbs of the H, as shown on the right in Fig. 720, a hydrogen vacuum tube so shaped affording the desirable primary spectrum for a practically unlimited time.

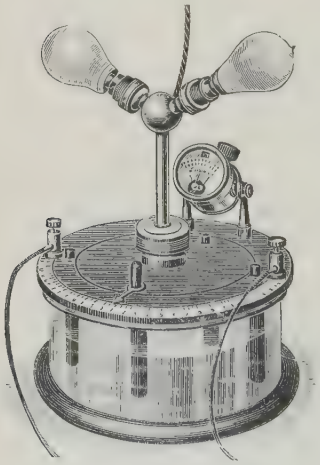


FIG. 721.—The Galvanoset.

A convenient arrangement for utilising the main supply of electricity, either continuous or alternating, of any voltage, for the immediate production of low-voltage currents from 0·5 to 100 volts, of the kind for which accumulators have usually been employed, is provided in the "Galvanoset" of the Medical Supply Association. It is shown in Fig. 721.

It consists of a circular glass vessel containing water, two fixed electrodes, and two movable electrodes. The current from the supply main enters at an upright central terminal and passes through two lamp resistances to the movable electrodes, and the circuit of utilisation is connected to the two terminals shown in the figure at the right and left margins of the vulcanite cover

to the vessel. When the four electrodes are 90° apart, as shown in the figure, the potential at the utilisation terminals is zero; but when the movable pair of electrodes are rotated from this position by movement of the rotatable part of the cover-plate which carries the indicator, a potential is obtained which varies as the displacement effected and is indicated by the circular scale. Reversal of the polarity of the utilisation supply is produced by moving the pointer in the opposite direction. A milliampère-meter with shunt winding is also carried above the vulcanite cover.

The best mercury and cadmium lamps are those devised by Dr. H. J. S. Sand,[1] the same principle and general construction being applicable to both, the cadmium being melted before use by extraneous heating by means of a Bunsen burner, and then acting like mercury does in the cold, the arc being struck by tilting. The lamp is constructed of quartz glass (fused silica), and its general shape is shown in Fig. 722. The success of the lamp is due to the discovery by Dr. Sand that an efficient vacuum-tight seal is afforded by metallic lead.

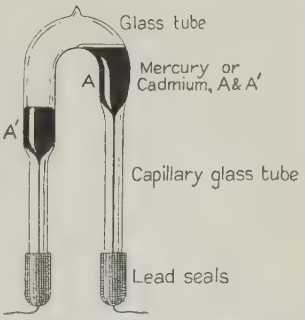


FIG. 722.—Dr. Sand's Cadmium or Mercury Lamp.

The lamp consists of a quartz tube bent into an inverted U in such a manner as to give rise to a short cathode chamber A and a long anode chamber A′. Each of these chambers is continued downwards as a thick-walled capillary through which a tungsten wire passes, the lead seals being filled at the ends of the legs. The lead is forced in the fused state, by atmospheric pressure, into absolute contact with the quartz and tungsten during the construction, filling up the ends so perfectly as to render them vacuum-tight. Considering first the cadmium lamp, the filling in of the cadmium is done through an upper attachment at the summit of the bend, not shown in the figure, as it is fused off on completion of the filling, the little projection at the top of the lamp indicating where the fusing off has occurred. A small amount of recently ignited zirconium oxide is first introduced at the top of the tungsten wires, where the chambers expand out of the capillaries; the oxide of zirconium prevents adherence of the cadmium to the quartz glass. The piece of cadmium is placed in a wire gauze cage contained in a side tube of the filling attachment referred to, the main tube of the attachment being connected to the pump. After exhaustion by the latter the cadmium is melted in its cage and the latter filters off all cadmium oxide, only allowing the pure metal to run into the lamp chambers, any occluded gases being at the same time eliminated. The attachment is then fused off at the oxy-hydrogen blowpipe, and the lamp is ready for use. It is best supported by means of a clamp holding one leg, and the necessary tilting to strike the arc after melting the cadmium can then be readily effected by rotating

[1] *Proc. Phys. Soc.*, 1916, *28*, 94.

the shank of the clamp in its boss head. The heating for the fusion should be done from the top by a Bunsen gas-burner. The lamp often lights up even before tilting. It is run on a 100 or 200 volts lighting circuit, with a back resistance adjusted to take a current of 5–7 ampères on short-circuit. Owing to the small upper chamber holding the cathode, metal distils into it from the hotter lower anode chamber, and drips back again once every two or three minutes, causing a slight flicker, which does not interfere at all, however, with the use of the lamp. The temperature of the lamp is maintained high enough to prevent any condensation of metal vapour on the quartz glass. The lamp may be kept burning for any length of time, and yields a powerful light, suitable for all the purposes described in this book, including spectroscopic, polarimetric, and interferometric work, as well as for calibrating the monochromatic illuminator as regards the positions of (circle readings for) the prism corresponding to the brilliantly outstanding red, green, and blue cadmium lines.

The mercury lamp is similar, liquid mercury simply replacing the cadmium and requiring no extraneous heating. The lead seals have proved a perfect solution as regards vacuum tightness, just as in the case of cadmium. A quartz glass mercury lamp of this character withstood a test of 500 hours intermittent burning quite unimpaired, and it affords a powerful light, yielding the green and violet mercury lines with great intensity and steadiness.

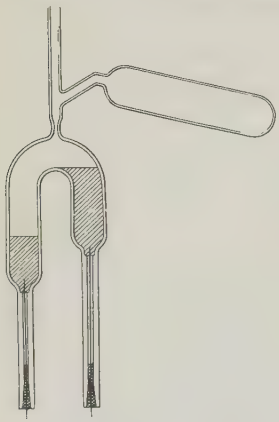


FIG. 722*a*.
The Bates Cadmium Lamp.

A cadmium vapour-lamp has also been described by F. Bates,[1] resembling the Sand lamp in all essentials, as will be clear from Fig. 722*a*, which represents it before the final sealing off. It is likewise constructed of fused quartz, and of 10 c.c. capacity. It is filled by distilling a cadmium-gallium alloy (2-3 per cent. gallium) from the quartz-glass bulb attached as shown to the side of the filling tube at the top of the figure; this alloying with gallium renders the cadmium soft and prevents any possibility of breakage on the solidification of the cadmium. The lamp works with 3 ampères at 110 volts, but is best with 7 ampères. Like the Sand lamp it furnishes a very intense source of red light of the wave-length 6438 Å.U.

Dr. T. M. Lowry[2] has pointed out a remarkable and very useful property of the mercury arc, as thus produced in a fairly wide quartz-glass tube, namely, the pinching together of the illuminating arc into a narrow thread only one-third of the diameter of the tube wide. This is a result of Faraday's law that currents travelling in the same direction attract one another, and it proves a very convenient feature of this lamp, as the brilliantly luminous thread acts as a slit for spectroscopic purposes, that is, it renders

[1] *Phil. Mag.*, 1920, *39*, 353.
[2] Royal Institution—Friday Evening Lecture, April 18, 1913.

the use of a slit not absolutely essential; and even when a slit is available and already present on the instrument in use, the brilliantly luminous thread just covers the slit without extravagant expenditure of energy, the source being of the same elongated shape as the slit.

A special short and compact form of the Cooper-Hewitt mercury lamp used for optical workshop lighting (the usual form being 4 feet long) is described by J. Guild.[1] The ordinary shorter form is useless for interference work with any but very thin films, owing to the high temperature to which it rises and consequent high mercury-vapour pressure, which causes broadening of the lines and interference bands. This defect is avoided in the special form now described, by blowing a large condensing bulb (5 inches in diameter) on the ordinary form above the positive electrode, as shown in Fig. 722*b*. The lamp is constructed by the Westinghouse Cooper-Hewitt Co. When taking a current of $2\frac{1}{2}$-3 ampères (not more than 5 in any case) the lamp produces fringes for the green mercury line 5461 Å.U. with as great a path-difference as 10 centimetres, and the illumination is very brilliant. The deviser of this lamp recommends the addition of a similar large bulb to the Sand cadmium lamp, and considers that the lamp would then be better fitted to afford interference bands for rays of long path-difference. The ordinary long Cooper-Hewitt mercury lamp is not subject to the defect above referred to, and interference bands in the green 5461 light have been produced of two decimetres path-difference.

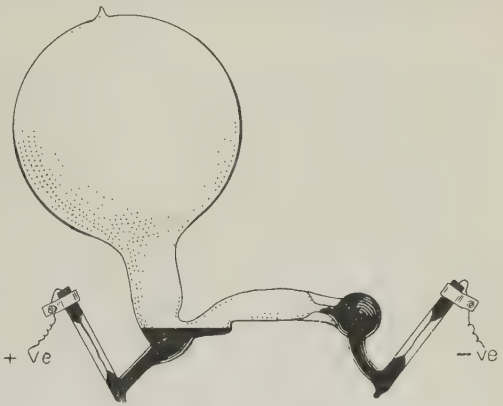


FIG. 722*b*.—The Cooper-Hewitt Mercury Lamp.

[1] *Proc. Phys. Soc.*, 1920, *32*, 341.

CHAPTER XLV

THE DETERMINATION OF EXTINCTION ANGLES BY THE STAUROSCOPE

The most efficient form of polariscope for the accurate determination of extinction angles is the "Stauroscope" belonging to the "Universal Crystal Apparatus" of von Groth, constructed by Fuess of Berlin. The polarising microscope may be used for preliminary or approximate work, as will be fully described in Chapter LIII.; but for accurate measurement no instrument has yet proved so satisfactory as the Fuess stauroscope. The optical tube which carries the large polarising Nicol is the same as that of the optic axial angle goniometer of the universal apparatus, but without the convergent system of lenses, and the same Nicol analyser is employed with both, but a different optical tube and other fittings are employed with it.

The stauroscope is shown in Fig. 723, partially in section, and later in Fig. 725 in position during a determination in monochromatic light, with the aid of the spectroscopic illuminator. It is essentially a polariscope arranged for parallel light, having wide optical tubes, large lenses for the parallelisation of the beam of light, and a large Nicol prism polariser, in order to transmit the maximum of light. Besides a Nicol analyser of smaller size, provided with a very small eye-hole to avoid parallax, and covered with a small slightly enlarging concave lens, the second or analysing tube is provided with a Calderon double calcite plate, a half-shadow compound plate resembling a bi-quartz, for enhancing the sensitiveness of the determination of the exact positions of extinction in the crystal plate.

From a strong base *a*, between the two claws of which an adjustable mirror *b* is carried, chiefly for use in white light observations, rises a column *c* of triangular section, carrying two sliders *d* and *e*, the lower *d* being capable of fixation at any convenient height, by means of the milled-headed clamping screw *f*, and the upper *e* being adjustable at any height by rack and pinion, the latter manipulated by the milled head *g*. Each slider carries one of the two wide optical tubes, which have a common axis, which is vertical when the apparatus is standing on its base as in Fig. 723. The lower tube *h* has an inner tube *i* carrying a doubly convex lens *j* at its lower end, and a similar one *k* at its upper end, the pair together furnishing a parallel beam of light, all of which has passed through the polarising Nicol *l*, in which the rays cross, and which has a minimum aperture of 1¼ inches. The inner tube carries a clamping ring *l'*, which has a V-shaped projection fitting in either of two corresponding

notches 45° apart in the lower edge of the outer tube. The ring is clamped on the inner tube in such a manner once for all that when the V fits one of the notches the plane of polarisation of the Nicol is arranged symmetrically to the stand, and corresponds to the zero mark of the vernier, which is fixed at the outer end of that diameter of the circle which is parallel to the line passing symmetrically between the claws of the stand.

About the upper end of the outer tube is carried the rotating divided circle *m*, as the silver bevelled flange of a rotatable cap or short tube *n*, which carries a special arrangement for the support of the crystal section-plate, which latter is cut or ground parallel to the symmetry plane when the crystal is monoclinic. The bevelled graduated silver limb *m* of the circle rotates over a silvered flange *o*, solid with the supporting ring *p*, which is carried at the end of the short arm proceeding from the slider *d*; the outer tube is screwed directly into this ring *p*, and the silvered flange *o* bears the vernier graduations on the front part of its horizontal surface. The circular table *q* forming the top of the cap is detachable, but when replaced always takes up the same position again, owing to its having a notch fitting about a pin in the annulus rim. The table is perforated by a rectangular central aperture, along one of the longer edges of which a straight strip of hard metal *r* is carried, the edge of which abutting on the aperture is a truly straight line, and the narrow surface is bevelled slightly out of the exact vertical plane so as to make the important upper straight-edge slightly overhang.

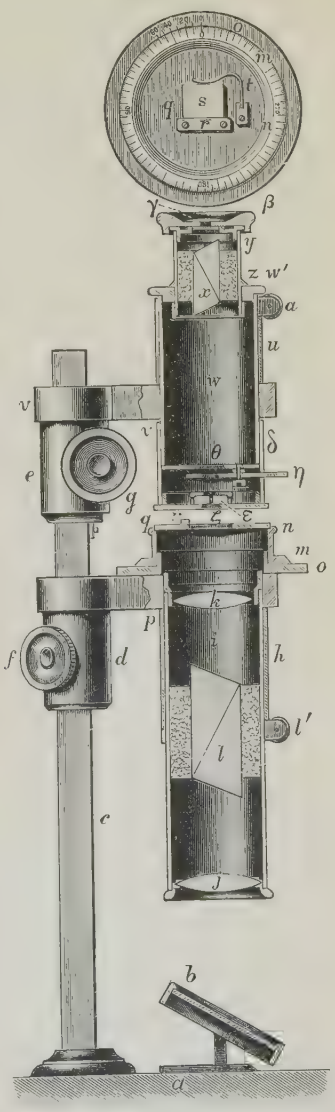


FIG. 723.—The von Groth Stauroscope as constructed by Fuess.

In some instruments this edge is very slightly curved (concave), in order to afford two-point contact only to the plane edge of the mount-plate presented to it; the line joining the two points, or the straight-edge itself when no curvature is given to the edge, is arranged so as to be exactly parallel to the right and left 90°-270° diameter of the circle, when the zero graduation is opposite the zero of the vernier, as shown in the separate upper part of Fig. 723, and also in Fig. 724. Against the straight-edge (or the two points of the curved edge) an especially truly planed and polished normal edge-face of a rectangular glass plate *s* is maintained pressed, during the determination of extinction, by a spring *t*, as shown in the upper part of Fig. 723. It is on this plate that the crystal-section is mounted with hard balsam dissolved in benzene. The normal edge-face in question of the glass plate is 2 millimetres wide, corresponding to the thickness of the plate, and is polished truly at 90° 0′ to the broad plate surfaces, so as to afford an excellent image of the goniometer

signal, the other three edge-faces being left rough-ground. The polished edge of the plate is marked in the middle near the position for the crystal with a deep round niche, which enables the light rays to get at the crystal faces during the measurement on the goniometer of the angles between the plate surfaces and crystal faces of reference.

The crystal is mounted on this glass plate so that one of the original natural faces —belonging to the ortho-zone if the crystal be of monoclinic symmetry, normal to the ground pair of faces parallel to the symmetry plane—is approximately parallel to this reflecting glass face. The angle between the two—for except by chance absolute parallelism cannot be attained by hand setting—can then be determined by actual measurement on the goniometer, and thus be used as a correction for the true position of the crystal face with respect to the direction of the 90°-270° circle graduation. Any slight error of setting of the straight-edge itself to the 90°-270° graduation is corrected by reversal of the glass plate and crystal, the latter then being below the plate and projecting through the aperture of the stage, and by taking a second series of stauroscopic observations for this position. The error is eliminated in taking the mean of the two observations, as well as any error of setting of the 90°-270° and 0°-180° diameters of the circle to the planes of vibration of the Nicols.

The upper optical tube consists of an outer tube u carried by the annular termination of the arm v proceeding from the slider e. Into the upper part of this tube slides an inner one w, terminating above in a thick flange w' with truly plane upper surface of silver, on which a radial zero mark is engraved. Within this tube at its upper extremity fits the analysing Nicol x, the supporting tube y of which carries about one-third from the bottom a bevelled silver circle z, fitting fairly tightly over the silvered top of the flange w'. The Nicol is thus rotatable and its position with respect to the zero mark indicated by its circle. Immediately below the flange a tightening collar a is fixed, bearing a V-projection capable of fitting in a corresponding notch in the upper rim of the outer tube u, and the collar is tightened at such a position that the zero mark then corresponds to that of the vernier of the circle plate o of the lower optical tube. Above the analyser there fits loosely a detachable shallow cap β, pierced at its centre by a circular aperture of only 3 millimetres diameter, and closed by a small concavo-convex lens γ. This is essential, for in order to obtain a sharp extinction the position of the eye must be maintained perfectly central. The lens also affords a slight enlargement of the field and of the crystal placed on the stage-plate.

When this inner tube w is pushed down into position in the outer tube u, with its collar projection properly fitted in the notch, about three-quarters of an inch of it projects below the annulus v of the supporting arm. Over this slips tightly from below a further short tube or lower cap δ, forming a detachable continuation of the outer tube. The lower end of this cap carries the stauroscopic plate ϵ for enhancing the sensitiveness of the determinations of extinction. In the author's instrument it is a Calderon double plate of calcite. It is constructed by cutting a rhomb of calcite along the shorter diagonal of the rhombohedron, the plane of cutting being thus a principal section containing the optic axis; from each half a wedge of the same angle is then ground, leaving the cut surface as one face of the wedge in each case; the two wedges then are cemented together by their other ground surfaces, after the latter have been polished, the thick end of one wedge being cemented to the thin end of the other, one wedge being thus rotated for 180°. A plate is then cut from the compound block thus obtained, at right angles to the plane of cementation, by cutting away the re-entrant angles of this artificial twin, so that when the plate is regarded normally the junction plane is seen in plan as a fine line. When placed between crossed Nicols, with this dividing line parallel to the vibration plane of one of them, such a plate shows an equal amount of extinction in each half, that is, the slight shade in each half is the same; for each is equally slightly removed, by the angle of the wedges, from the principal-section plane. If a crystal plate be interposed,

on its glass plate laid on the stage at the top of the lower optical tube, that is, at ζ, the two halves will at once show a marked difference of colour tint or brightness, unless the extinction directions of the crystal coincide exactly with those of the Nicols. Hence, when such a difference appears, the crystal and stage must be rotated along with its divided circle until equality of tint or intensity is again restored. This angle of rotation is the difference between the setting of the crystal on the plate, which has been goniometrically determined with reference to an actual face of the crystal, and the extinction direction. The angle of extinction with reference to the face in question is thus the sum or difference, according to the direction of rotation, of the angles found respectively on the stauroscope and the goniometer.

In order to screen off as much extraneous light as possible a rotatable diaphragm carrying four apertures of different sizes is placed at η, so that the circular aperture of the fixed diaphragm θ can be more or less constricted at will, and the crystal thus made to occupy most of the visible field. The inner tube w is slotted for half an inch at its lower end, to take a pin screwed so as to project through the tube δ of the cap, at such a position as brings the dividing line of the Calderon double-plate parallel to the plane of vibration of one of the crossed Nicols.

Thus when all is in position the conditions are as shown in Fig. 724. The crystal edge of reference c, the plan or trace of an existing face, is either parallel to the straight edge ab and to the 90°-270° graduation and to the plane of vibration of the corresponding Nicol, or makes a known (measured) angle therewith.

Before carrying out a determination of extinction, the polarising Nicol is arranged once for all so that its vibration direction is as nearly as possible parallel to the line joining the centre of rotation of the circle to the 0° mark of the fixed vernier o.

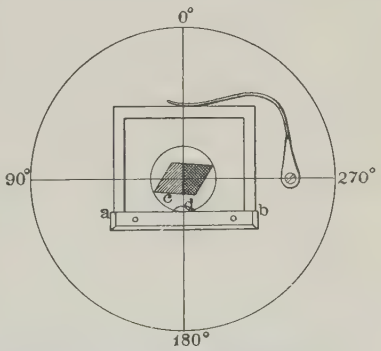


FIG. 724.—Conditions in the Stauroscopic Determination of Extinction.

The analyser is then arranged with its vibration direction perpendicular to this position, so that the maximum darkness of field is produced when the Calderon double-plate is removed and nothing interposes between the two Nicols. The cap containing the Calderon plate is then replaced in position at the lower end of the tube w, so that the pin fits in the slot and is pushed home to the end of the latter. Two of the rectangular glass plates should, the day previously, have had the pair of ground and polished crystal section-plates mounted on them, near the ground-away niche d (Fig. 724), for then when the plate is placed in position against the straight-edge, and the circular diaphragm-aperture of suitable size adjusted, the crystal will appear centrally in the field of view on looking through the analyser, as shown in Fig. 724. The angle α made by the crystal face, which has been arranged approximately parallel to the truly plane glass edge-face, with the latter, should then be measured on the goniometer, just before placing it on the stauroscope stage. Before thus placing it, moreover, the

adjustment of the Calderon double-plate should be looked to, and the fact verified that the two halves are absolutely equally in half shadow, that is, equally only very slightly lighted, almost dark, under the crossed Nicols. After having done this efficiently once, it will be found on subsequent occasions that it is only the analyser which is not absolutely at its zero graduation if the lighting of the Calderon plate is not evenly distributed.

On now placing the glass plate and its mounted crystal section-plate in position on the circle-cap, against the straight-edge, and sliding it slightly, if necessary, while pressed against the straight-edge by the spring, until the crystal appears centrally situated in the field, the crystal will be seen to be sharply divided off into a bright half and a dark half, by the line of junction of the two halves of the Calderon double-plate, unless the position of the crystal is by chance adjusted near to that for extinction. On rotation of the circle, which involves that of the whole cap and crystal stage, the difference of brightness or tint of the two crystal halves will be either still further accentuated or diminished, according to the direction of rotation. The direction for diminution being then known, the circle is turned in that direction until equality of depth of greyness or absolute match of colour tint is shown in the two halves, no difference whatever being apparent between them. This position, with a good crystal, is capable of detection in the author's instrument with certainty to 5 minutes of arc. It is useless to expect to pass beyond this degree of accuracy, or even to attain so sharp a determination in the case of a poorer crystal, with any known form of sensitiveness enhancer, as the result of a single determination. Hence, half a dozen different settings should be made to the extinction position, and the mean taken, when a somewhat closer approximation will be reached.

When the position of extinction has thus been found, what has really been achieved is that the two perpendicular directions of extinction (for the same character of extinction occurs at 90° to the position found) have been ascertained with reference to the planes of vibration of the Nicols, assuming that the 0°-180° and 90°-270° diameters of the circle respectively have been set truly parallel to the planes of vibration of the Nicols, which, however, is not the fact, for this setting can at the best have been only approximately achieved experimentally. Moreover as regards defining the extinction position crystallographically, with respect to the reference face, the angle of rotation on the circle from the 0°-180° diameter, that is, from the zero of the circle as read by the fixed vernier, gives the extinction direction with respect to the straight-edge and reflecting edge-face of the glass mount-plate, and not with respect to the reference face. But as the small angle α enclosed between the glass edge-face and the crystal face arranged approximately parallel to it has previously been measured on the goniometer, it is only necessary to subtract it from or add it to the mean stauroscopic extinction angle just found, according as the angle through which the crystal has been rotated includes this small angle or is adjacent and additional to it, in

order to arrive at the extinction angle with respect to the reference face. No mistake in applying this correction can be made if the direction of the correction angle is first of all carefully observed, and the graduation of the circle appreciated which really corresponds to the setting of the reference crystal-face itself (rather than the straight-edge and glass edge-face) to the zero position. Indeed, to avoid the possibility of any such mistake in the sign of the correction, it is not a bad plan so to mount the crystal that the reference face makes a decided visible angle with the edge-face of the glass mount-plate. Another precaution to remember is that, in measuring the correction angle, the glass plate must be adjusted truly horizontal on the goniometer axis, assuming the reference face to be one in the ortho-zone of a monoclinic crystal, which is thus perpendicular to the section-plate parallel to the symmetry plane, and to the glass mount-plate. For other more complicated cases special instructions will presently be given.

In order to eliminate finally the possible error in setting the plane of the polarising Nicol parallel to the diameter containing the zero of the vernier, the glass plate is then reversed, so that the crystal is below it instead of above it, but with the reflecting edge-face of the glass plate still pressed by the spring against the straight-edge. A second series of half a dozen adjustments to extinction should again be made, and the corresponding readings recorded and their mean taken. This is then independently corrected for the setting of the crystal on the mount, the small angle α being added or subtracted as the case demands. The mean of the two values thus obtained, for the reversed positions of the crystal above and below the plate respectively, is then taken as the true extinction angle ϕ for that particular crystal.

Precisely similar procedure is adopted for the observations with the second (duplicate) crystal plate, and the mean of the results for the two crystals, which should not differ by more than a very few minutes, is accepted as the true extinction angle for any plate of this crystalline substance having this orientation. When the crystals are monoclinic, the result is thus to afford the directions of extinction in the symmetry plane, the section-plates having been ground parallel thereto; hence, they are really the directions of the two axes of the optical ellipsoid lying in the symmetry plane.

Now as the two perpendicular extinction directions — in such a plate parallel to the symmetry plane of a monoclinic crystal or to a principal plane of the optical ellipsoid of a triclinic crystal, that is, the directions of two of the three principal axes of the optical ellipsoid — are dispersed for different wave-lengths of light, it is always advisable, and imperative when this dispersion exceeds 5′, that the observations should be made in monochromatic light. Usually it suffices to employ sodium light for extinction determinations, the most intense one procurable being used, such as is afforded by a fan-tail Bunsen burner into the broad and high flame of which several little platinum boats containing a bead of sodium salt are introduced, or any other of the many laboratory arrangements now available for producing an intense sodium

flame. Better still, however, is the monochromatic illuminator described in the last chapter, with which the determinations should be made for red C- and greenish-blue F-hydrogen light as well as for sodium light, the light of all these three wave-lengths being supplied directly from the illuminator, using the electric lantern as source of light. A convenient mode of supporting the stauroscope horizontally in front of the ground-glass diffuser of the spectroscopic illuminator is shown in Fig. 725. Excellent illumination is obtained by this mode of procuring the necessary monochromatic light, for not only these three, but any other desired wave-lengths whatsoever.

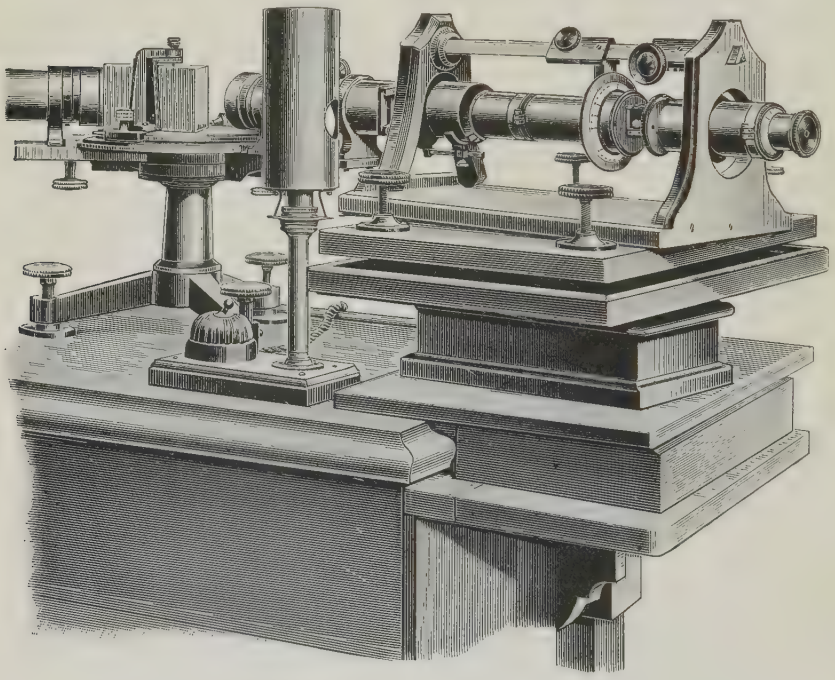


FIG. 725.—Determination of Extinction Angles in Monochromatic Light.

The mode of carrying out such an observation of extinction will now be illustrated by a concrete example, that of ammonium magnesium sulphate, the substance taken in Chapter XVII. as an instance of characteristic monoclinic symmetry. Sodium light here suffices as the dispersion of the axes of the optical ellipsoid is extremely small.

Determination of Orientation of the Axes of the Optical Ellipsoid of Ammonium Magnesium Sulphate, $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$.—The section-plate parallel to the symmetry plane $b = \{010\}$ is represented in Fig. 726. Its edges were formed principally by the two pairs of parallel faces $a = (100)$ and $a = (\bar{1}00)$, and $c = (001)$ and $c = (00\bar{1})$, the latter forming the long edges, and also subsidiarily by smaller faces of $r' = (201)$ and $r' =$

(201). Strips of these six faces were left along the margin of the plate, and as they all belonged to the ortho-zone parallel to the symmetry axis b (the normal to the plate) they were all perpendicular to the plate. The face $c = (001)$ afforded a particularly good single reflection of the goniometer signal, and hence was chosen as the reference face. The crystal was mounted with hard balsam dissolved in benzene, so that this face made a small visible angle with the reflecting edge-face of the glass mount-plate. After drying for a day to harden the balsam cement this angle α was measured on the goniometer. The stauroscopic measurements were then made, first with the mount laid on the stage with the crystal above, and afterwards with the mount reversed and the

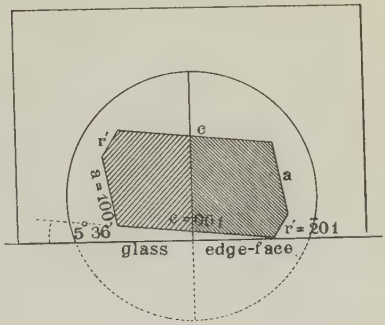
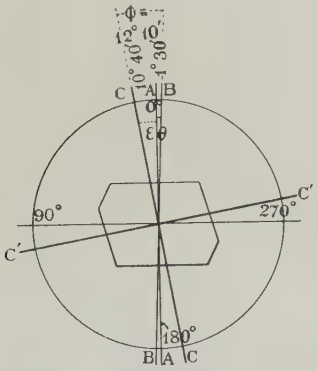
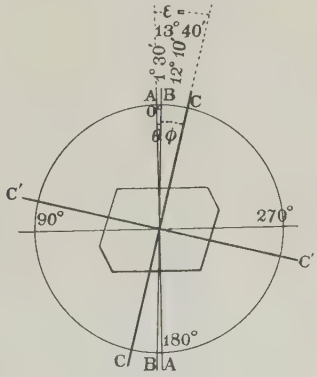


FIG. 726.—Section-plate of Ammonium Magnesium Sulphate as seen in Stauroscope.



Crystal above

FIG. 727.



Crystal below

FIG. 728.

Conditions in Determination of Extinction Directions of Ammonium Magnesium Sulphate.

crystal below. The results were as under. Figs. 727 and 728 graphically express the conditions in the two series of observations.

Angle of inclination α of c-face to glass edge-face, 5° 36′.

Determinations of Extinction Angle.

Crystal above glass.	Crystal below glass.
4° 56′	8° 6′
5 6	8 8
5 6	7 54
4 52	8 4
5 6	8 14
5 12	7 58
Mean 5° 3′	Mean 8° 4′
+α 5 36	+α 5 36
Apparent extinction angle referred to normal to c=(001). 10° 39′	Apparent extinction angle referred to normal to c=(001). 13° 40′

True (mean) extinction angle, 12° 10′, with respect to normal to $c=\{001\}$.

This extinction angle of 12° 10′ made with the normal to the basal plane, $c=\{001\}$, lies in the direction behind the normal, as will be clear from Fig. 729, which is the type of figure which should be drawn to express graphically the results for every substance investigated.

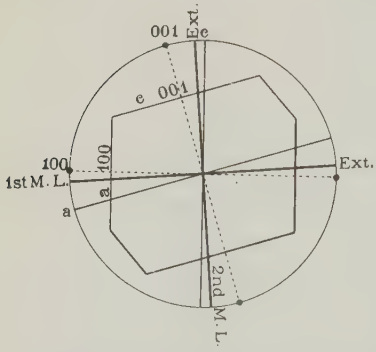


Fig. 729.—Extinction Directions in Plate of Ammonium Magnesium Sulphate Parallel to Symmetry Plane.

The difference between the two results for the reversed positions of the crystal, 10° 39′ and 13° 40′, namely, 3° 1′, is double the difference between the setting of the plane of polarisation of the polarising Nicol and the zero diameter of the fixed vernier circle. The correction angle itself is thus 1° 30′. That is, the true circle reading for one of the vibration directions of the two Nicols (that of the analyser when crossed to the polariser with maximum darkness of field) is 358° 30′ instead of 360° 0′ (the same as the zero mark 0° 0′), when the zero marks of the fixed vernier and rotatable circle are opposite each other. This error of 1° 30′ in the placing of the zero to the plane of vibration is thus eliminated by actual experiment, but when it is known it may be used directly as a correction to the apparent extinction angle. It is much better, however, to eliminate it thus experimentally, for it varies slightly with the setting of the analysing Nicol for production of the most perfect dark field, which can of course only be achieved within the limits of the usual few minutes. The correction α of 5° 36′ for setting of the crystal plate on the mount is clearly shown in Fig. 726, but is ignored in Figs. 727 and 728 to save unnecessary complication, the crystal being assumed in these latter figures to be set with its c-face parallel to the edge-face of the glass mount.

In Figs. 727 and 728 the direction A is that of the 0°-180° diameter

of the circle. B is the true direction of vibration of the analyser and perpendicular to the vibration direction of the polariser, when the 0° reading of the circle is opposite the 0° of the vernier (which is immovably fixed with respect to the polariser). C and C′ are the extinction directions in the crystal. The correction angle of 1° 30′ for the true position of the Nicols is θ; ϵ is the apparent extinction angle, and is the angle actually read off, corrected by adding or subtracting, in this case the former, the angle α between the reference crystal face and the glass edge-face. Lastly, ϕ is the true extinction angle, and is the sum of θ and ϵ in the case of Fig. 727, with the crystal above the plate, but the difference of ϵ and θ in the case represented by Fig. 728, with the crystal reversed underneath the glass plate.

A second section-plate parallel to the symmetry plane, ground from another crystal of ammonium magnesium sulphate derived from a different crop, afforded the value 12° 5′ for the true extinction angle of ammonium magnesium sulphate in the symmetry plane, with respect to the normal to the same face $c=(001)$.

Hence, the author has accepted the mean of the two values derived from these two different crystals, 12° 8′, as the true extinction angle, that between the a axis of the optical ellipsoid (indicatrix), the second median line, and the normal to the basal plane $c=(001)$, the direction being behind the normal and near to the vertical axis c of the crystal, as shown in Fig. 729.

This will be the usual method of determining the extinction directions of a monoclinic crystal, for it is rare to find absolutely no faces developed in the ortho-zone, suitable for reference faces. Occasionally, however, it will happen that there are no such faces, and with triclinic crystals more frequently, although the plate investigated is often very conveniently ground perpendicular to a pair of well-formed faces. One ought to be prepared to meet such cases of greater difficulty, and the following method of dealing with them is the simplest and most satisfactory.

Suppose Fig. 730 to represent the glass mount-plate—g being the upper surface of the plate and g_1 the truly plane-polished edge strip—with such a monoclinic crystal section-plate parallel to the symmetry plane mounted on it, of which c is the upper ground and polished surface and c_1 is the face of a principal form inclined to two axes, a prism face such as (110) or (011), for instance. The angle $c:c_1$ is measured on the goniometer, the edge cc_1 being adjusted for the purpose, and the little niche in the centre of the glass edge gg_1 has been cut to admit the light rays more fully for the purpose, for if the crystal plate be thin the glass edge otherwise gets in the way. During this measurement it will probably be noticed that the goniometrical signal-image from the glass surface g is coincident with that from c; it should be so if the crystal plate has been truly ground parallel-sided and evenly cemented with only a thin film of balsam. But unless the edge

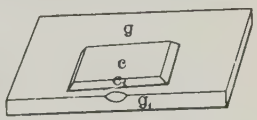


FIG. 730.

cc_1 has been set truly parallel to the edge gg_1 during the cementing, the images from c_1 and g_1 will not be in the same zone $[cc_1]$, that from g_1 appearing above or below in the field when the images from c and c_1 are adjusted to pass through the intersection of the spider-lines on rotation of the goniometer axis. The object is to find the mutual inclination of the two zones $[cc_1]$ and $[gg_1]$, for this is the same as that between the crystal and glass edges cc_1 and gg_1; this correction angle is lettered α as usual. Let the measured crystal angle $c : c_1$ be γ. We have first to find the angle δ which the rays reflected from c_1 make with the plane of the reflections from g_1, c, and g. Then Websky and Liebisch have shown that the desired small angle α can be calculated at once from the formula :

$$\sin \alpha = \frac{\sin \delta}{\sin \gamma \sqrt{2}}.$$

A very simple way of measuring δ is to set the telescope of the goniometer at exactly 90° to the collimator, by first placing it in the same straight line, so that the signal seen directly through the telescope and collimator is adjusted to the crossed spider-lines, and then rotating it 90°; we then know the angle of incidence, which will obviously be 45°. The ordinary Websky signal-slit is replaced by the alternative signal consisting of a small central circular hole, and the crossed spider-lines of the telescope are arranged as in Fig. 731, at 45° to their usual position, by rotation of the eyepiece for 45°; a second V on the collar of the eyepiece tube at 45° to the one usually employed, and fitting to the same usual notch in the outer tube, facilitates this adjustment. The images from c and c_1, the adjusted faces of the crystal, will still pass through the centre of the field on rotating the circle and the crystal-holder which it carries, one of them, say c, being shown adjusted at the centre in Fig. 731. But g_1 will pass either above or below the centre, as shown passing above in Fig. 731, its path being dotted because c and g_1 will obviously not be visible in the field at once, owing to the considerable angle between them. If we adjust the g_1, image first to one spider-line and then to the other, and take a circle reading for each such adjustment, the difference of the two readings will be δ. For it is half the observed angle of sweep of the ray between the adjusted position of the image g_1 on the right and that on the left, a reflected ray moving through twice the angle of movement of the surface reflecting it, which latter is that recorded by the circle readings. If we draw a perpendicular cN to the line of passage g_1Ng_1, then, the angles at g_1 and c being 45°,

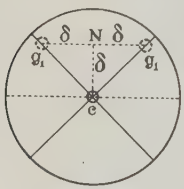


FIG. 731.

$$g_1N = \tfrac{1}{2}g_1Ng_1 = cN = \delta.$$

That is, cN is the desired angle δ of deviation of the rays out of the zone $[cc_1]$, and is at once afforded by the difference of the two readings

for the adjustment of g_1 to the two spider-lines as shown in Fig. 731. Hence, as we now know both δ and γ from direct measurement, we can calculate α by means of the formula.

As an aid to the calculation the following table has been prepared by Liebisch [1] and von Groth [2] in which the values of α are given for every 10′ of δ up to 3°, beyond which it is not required, and 5° or 10° of γ between 20° and 90°.

VALUES OF THE STAUROSCOPIC CORRECTION ANGLE α.

	γ=20°.	=25°.	=30°.	=35°.	=40°.	=50°.	=60°.	=70°.	=80°.	=90°.
δ=0° 10′	0° 21′	0° 17′	0° 14′	0° 12′	0° 11′	0° 9′	0° 8′	0° 8′	0° 7′	0° 7′
20	0 41	0 33	0 28	0 25	0 22	0 18	0 16	0 15	0 14	0 14
30	1 2	0 50	0 42	0 37	0 33	0 28	0 24	0 23	0 22	0 21
40	1 23	1 7	0 57	0 49	0 44	0 37	0 33	0 30	0 29	0 28
50	1 43	1 24	1 11	1 2	0 55	0 46	0 41	0 38	0 36	0 35
1 0	2 4	1 40	1 25	1 15	1 6	0 55	0 49	0 45	0 43	0 42
10	2 25	1 57	1 39	1 27	1 17	1 5	0 57	0 53	0 50	0 49
20	2 45	2 14	1 53	1 39	1 28	1 14	1 5	1 1	0 58	0 57
30	3 6	2 31	2 7	1 51	1 39	1 23	1 13	1 8	1 5	1 4
40	3 27	2 47	2 21	2 3	1 50	1 32	1 22	1 15	1 12	1 11
50	3 48	3 4	2 36	2 16	2 1	1 42	1 30	1 23	1 19	1 18
2 0	4 8	3 21	2 50	2 28	2 12	1 51	1 38	1 30	1 26	1 25
10	..	3 38	3 4	2 40	2 23	2 0	1 46	1 38	1 33	1 32
20	..	3 54	3 18	2 53	2 34	2 9	1 54	1 45	1 41	1 39
30	..	4 11	3 32	3 5	2 45	2 18	2 2	1 53	1 48	1 46
40	..	..	3 46	3 17	2 56	2 28	2 11	2 0	1 55	1 53
50	..	..	4 1	3 30	3 7	2 37	2 19	2 8	2 2	2 0
3 0	..	..	4 15	3 42	3 18	2 46	2 27	2 15	2 9	2 7

As an example of the use of the table, and in proof of the accuracy of the method, the case of a monoclinic crystal may be quoted, in which the calculated angle could be actually measured and confirmed, the angle between c and c_1 being 90°, an excellent face in the ortho-zone perpendicular to the symmetry plane being developed. The actual angle between c_1 and g_1 was measured directly on the goniometer, as usual when such a face perpendicular to the plate is present, that is, in the same zone with g_1 when the glass plate and crystal section-plate are horizontal, perpendicular to the goniometer axis. This angle $c_1 : g_1$ was found to be 2° 6′. The crossed spider-lines were then rotated 45°, by rotating the eyepiece so as to fit the second V of its collar into the notch of the outer telescope tube, and the Websky signal replaced by the hole signal; the mount-plate with its crystal was next arranged vertically, and the image from g_1 (for either c_1 or g_1 may be so centred) adjusted to pass through the intersection of the crossed spider-lines on rotation of the goniometer axis with the crystal-holder. The image from c_1 was then immediately above that from g_1, just sufficiently in the field to be able to be placed in succession to the two diagonally crossed spider-lines, where they nearly reached the margin of the circular field.

[1] *Zeitschr. für Kryst.*, 7, 304.
[2] *Physikalische Krystallographie*, 4th ed. (1905), p. 734.

The angle passed through on rotating the circle and crystal-holder between these two positions was 2° 55′, which was thus the value of δ. Looking out from the table the angle α corresponding to $\delta = 2° 55'$ and γ (the angle between the two crystal faces c and c_1) $= 90°$, we find it half-way between 2° 0′ corresponding to $\delta = 2° 50'$ for $\gamma = 90°$, and 2° 7′ corresponding to $\delta = 3° 0'$ for $\gamma = 90°$, that is, 2° 4′. This is only 2′ removed from the measured value 2° 6′, and thus verifies the table by direct experiment.

The polarising microscope with rotating divided stage and rectangularly crossed spider-lines at the eyepiece focus, can be used very conveniently for preliminary determinations of extinction, the reference face of the crystal being set to either of the cross-wires, one of which corresponds to the zero graduation of the rotating stage-circle, the Nicols being crossed. A special chapter, LIII., will be devoted to the use of the crystallographic microscope, including its use as stauroscope, and other forms of sensitiveness-enhancing plate than the Calderon double-plate will there be dealt with The methods which have been devised for determining the extinction directions in very small, even microscopic, crystal plates will also be described, including the use of such results in ascertaining the positions of the optic axes and the axes of the optical ellipsoid, even when derived from section-plates or thin crystals of any orientation whatsoever. For the purposes of the original investigation of substances the crystals of which can be procured of a size as large as that of a pin's head or larger, somewhat larger in preference, say that of a small pea, the stauroscope as described in this chapter is the best instrument to employ, in accordance with the methods here recommended.

Norremberg's Doubler.—A simple form of polariscope designed originally by Norremberg, although superseded for accurate measurement by the stauroscope just described, has such useful properties in qualitative and demonstration work, particularly in its original form for the examination of thin films such as those of mica and gypsum, as to merit special notice before concluding this chapter. It combines a Nicol prism, used as analyser, with a bundle of glass plates as polariser. It is shown in Fig. 732 in its original form, and in Fig. 733 as constructed in its modern form by Fuess. The outer mirror a of the two hinged mirrors a and b of the Fuess apparatus, or the similar one constructed by Steeg & Reuter, at the base of the apparatus, is an ordinary silvered mirror, by which the light rays can be directed at the polarising angle on to the second mirror b, which consists of the bundle of glass plates, from which the polarised light is reflected upwards into the instrument. The slider c carries a short tube d terminating above in a rotating divided stage e for the crystal object, below which is the lens for parallelising the light rays, and which can be supplemented by a convergent system, including a hemispherical condensing lens just under the object plate, when convergent light is required. The longer optical tube f, supported by the arm g projecting from the top of the vertical column h, carries a lens system which acts either as a low-power micro-

scope for parallel light, or, with the addition of a convergent system similar to the lower one, for collecting the rays converged by the latter, and enabling the interference figures in convergent polarised light to be clearly viewed. The Nicol prism analyser k is carried at the top of a further short flanged tube l, in which it is rotatable, and which is pierced by a slot m for the insertion of a quartz wedge or a quarter undulation mica plate. The instrument includes a very wide angle of field, both optic axes of crystals possessing apparent optic axial angles 2E of as much as 130° being completely visible with their ring systems.

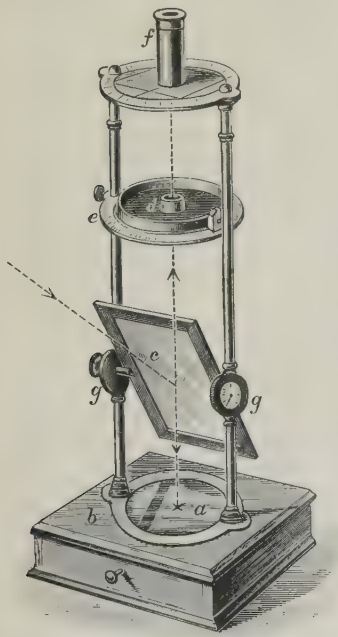


FIG. 732.—Norremberg's Doubler.

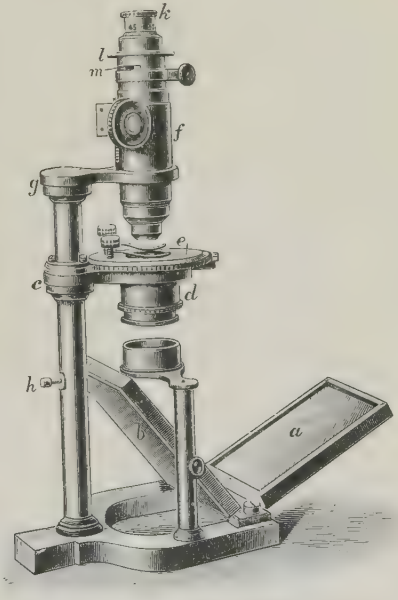


FIG. 733.—Modern Form of Norremberg's Doubler as constructed by Fuess.

In the earlier form in which Norremberg invented it, shown in Fig. 732, the silvered mirror a is laid on the basal box b of the apparatus, and the bundle of plates is replaced by a *single* plate of glass c carried in a rectangular frame. The rays of light are arranged to fall on this plate at the polarising angle, $56\frac{1}{2}°$, and so as to be reflected perpendicularly downwards to the mirror, from which they are reflected upwards to the object d on the stage e above the glass plate, and through the Nicol prism analyser f to the eye, passing through the glass plate on the way. The latter thus acts like the glass plate of the Gauss ocular or Becker fitting shown in Fig. 24 (page 41).

A small divided circle g is arranged at each end of the axle of the frame carrying the glass plate, in order to indicate the angle of tilt.

When the crystal plate under investigation is laid on the stage, the polarisation phenomena of an ordinary polariscope are afforded. But when it is laid on the silvered mirror, or for greater convenience on a second stage inserted between the mirror and the inclined glass plate, the rays of light then traverse it twice, both in going to and in returning from the mirror, and the phenomena observed are those of a plate of the crystal of double the thickness, thus giving the name "doubler" to the instrument. Provided the crystal does not fill the whole field, two images of it will be seen, a larger one, the directly viewed image, and a smaller one reflected from the mirror, and this latter will show effects as if the plate were of twice the thickness.

A simple addition to the polarising microscope of an inclined (rotatable) glass plate fitting, such as is used for the illumination of opaque objects under the microscope, converts the latter into a very efficient "doubler."

CHAPTER XLVI

THE DETERMINATION OF THE REFRACTIVE INDEX OF CRYSTALS BY THE 60°-PRISM METHOD, AND OF MOLECULAR REFRACTION

By far the most satisfactory and accurate method of determining the refractive index or indices of a crystal is that of the 60°-prism, provided such a prism—if the crystal be cubic in symmetry and therefore singly refractive, or if it be uniaxially doubly refractive (when one properly orientated prism also suffices)—or the necessary pair of prisms if the crystal be biaxially doubly refractive, can be cut or ground out of the crystal. This can always be done, unless the crystals are only of microscopic size, by means of the cutting and grinding goniometer described in Chapter XLIII. and shown in Fig. 702, employing the special crystal-adjusting apparatus for use in the preparation of 60°-prisms there described. Even soft and brittle crystals can be successfully ground into prisms with this most useful apparatus, with one setting of the crystal on the crystal-holder, and the author has frequently prepared satisfactory prisms out of crystals no larger than the head of a pin. Crystals of the size of a small pea are the most suitable and convenient, when available. But even much larger crystals may be employed, and correspondingly larger prisms prepared, when the crystal is an internally homogeneous and perfectly transparent one.

Isotropic (Cubic) Crystals.—When the crystal is one belonging to the cubic system, and therefore isotropic, a single 60°-prism will afford the unique refractive index μ, and it may be orientated anyhow in the crystal. The case is the simple one of an isotropic substance described on p. 830, a cubic crystal or glass, for instance, behaving similarly in this respect. But in the original investigation of an apparently cubic substance, the careful observer would prepare at least three such 60°-prisms from the same crystal, and orientate them so that the bisecting plane was parallel to each of the three pairs of faces of the cube in turn, in order to confirm that the refractive index is really identical for the directions of all three principal axes of the crystal. A fourth 60°-prism, cut obliquely, should also be ground, in order to establish finally the fact that whatever be the direction in which the light travels through the crystal, the refractive index corresponding is the same.

Any and all of these prisms, when arranged for minimum deviation,

will yield only a single image of the "Websky" signal-slit of the goniometer-spectrometer, when the latter is illuminated by monochromatic light, or a single corresponding spectrum when white light is employed, just as in the case of a glass prism; the angle of the minimum deviation of this single image, for each of the six usual wavelengths of light, together with the accurately measured value of the angle of the prism—as determined by the ordinary goniometrical method of measurement of the angle between two faces, after having adjusted the refracting edge between those two faces with the aid of the goniometrical centring and adjusting movements—afford all the data necessary for the calculation of the unique index of refraction. Moreover, the image remains constant and permanent when a Nicol prism is attached in front of the eyepiece and rotated, the only difference of intensity observed being that due to polarisation by reflection at the incident face of the prism, the reflected rays being more or less polarised in the plane of incidence, and the refracted beam reaching the eye in the absence of a Nicol being partially polarised perpendicularly to the plane of incidence.

The direction of vibration of the refracted polarised light is thus parallel to the plane of incidence, the horizontal plane when the prism is set up as usual on its triangular base. Consequently, when the vibration direction of the Nicol is also horizontal these vibrations get through unaffected, but when the Nicol is rotated a right angle so as to bring its vibration direction vertical they are extinguished, so that the ordinary refracted light only (that larger part which had never been polarised) gives rise to the vertically polarised light produced by the Nicol. Thus it is that the light received from the prism, when the Nicol is also introduced in front of the telescope eyepiece, appears less intense when the Nicol is at 90° (vibration direction vertical) than when it is at 0° (vibration direction horizontal).

Uniaxial Crystals.—If the crystal be of tetragonal, hexagonal, or trigonal symmetry it will possess two extreme refractive indices, the ordinary ω corresponding to light vibrating along all directions perpendicular to the principal (trigonal, tetragonal, or hexagonal) axis, the optic axis, and the extraordinary ϵ corresponding to light vibrating parallel to the optic axis. Which of the two is the greater index depends on the sign of the double refraction; in positive crystals it is ϵ, and in negative ω.

We have to remember the following salient facts as regards the refractive indices of uniaxial crystals. Rays travelling along the optic axis, the principal crystallographic axis, afford only one refractive index ω, corresponding to vibrations in the circular section. Any ray passing obliquely through the crystal and its imaginary optical ellipsoid of revolution is resolved into two component rays. One of these, the so-called ordinary ray, is plane-polarised in the principal section (that containing both the direction of the ray and the optic axis) and vibrates perpendicularly thereto along a radius of the circular section. Whatsoever be the position of the ray this component consequently always gives the same index of refraction, namely, ω. The other, the extraordinary

ray, differs in direction of vibration and in refractive index with the direction of the ray, and the difference from the refractive index ω of the ordinary ray is at its maximum corresponding to the extreme value ϵ, the quantity to be determined, when the ray is transmitted in the circular section itself and vibrates parallel to the optic axis. The practical task is thus to determine ω and ϵ. Their difference is the measure of the double refraction.

A single prism will enable both ω and ϵ to be determined, provided it be cut or ground either so that the refracting edge is parallel to the optic axis, or else so that the refracting edge is perpendicular to the optic axis and the plane bisecting the refracting angle of the prism is parallel to the axis. That is to say, the bisecting plane of the prism must contain the optic axis, either as the refracting edge itself or as the perpendicular to that edge. These two varieties of prisms have both been fully described in Chapter XXXIX. discussing the passage of light through uniaxial crystals, and illustrated in Figs. 617 and 618 (p. 839).

Such a prism, when arranged for minimum deviation, and when the goniometer-spectrometer is illuminated by monochromatic light, instead of yielding a single image of the Websky signal-slit as in the case of a cubic crystal or glass, affords two such refracted images (see Fig. 736, p. 998), which are the more separated the greater the amount of the double refraction and the greater the angle of the prism. The double refraction is rarely so large as to prevent both being simultaneously visible in the field of view of the telescope. When the Nicol prism is in position in front of the eyepiece of the latter, as it always should be when prisms of doubly refracting crystals are under investigation, it will be found that one of the two images extinguishes absolutely when the Nicol is arranged with its plane of vibration at 0°, and the other also perfectly when the Nicol is rotated a right angle to its 90°-graduation. Both images will be visible at the 45° intermediate position of the Nicol. The image which is in view when the Nicol is at 90° is usually weaker in intensity than the other which is seen at its maximum intensity when the Nicol is at 0°, owing to the light entering the crystal being partially already polarised at the reflecting surface, apart from the polarisation due to double refraction, with vibrations in the horizontal plane of incidence. This somewhat weaker 90°-image is due solely to the double refraction and corresponds to vibrations parallel to the vertical refracting edge of the prism. The stronger one which is visible at the 0°-position of the Nicol corresponds to light vibrating perpendicularly to the edge but also in the bisecting plane. For the light passing through the prism parallel both to the imaginary triangular base and to the imaginary symmetrical third face (it being obviously unnecessary to cut these surfaces), as is always the case when the prism is arranged for minimum deviation, divides into two rays, both vibrating in the plane at right angles to the direction of transmission (the plane bisecting the refracting angle of the prism), the one along the vertical principal axis (optic axis) of the crystal and the other along the direction perpendicular thereto. That is, the two rays vibrate respectively parallel to the two axes of the optical indicatrix;

one of these is the optic axis and the other may be anywhere in the circular section of the indicatrix, the latter being an ellipsoid of revolution in the case of a uniaxial crystal. The former ray vibrating parallel to the optic axis gives ϵ, and the other vibrating parallel to the circular section gives ω. Which of the two corresponds to light vibrating parallel to the refracting edge of the prism depends, of course, on which of the two alternative modes of cutting the prism has been adopted. The author's practice is to prepare six such prisms, three of each mode of cutting, in order to eliminate, in taking the mean values of all the results, all possible experimental or structural errors, which usually only affect one or two units in the fourth place of decimals.

The image which is nearer to the direct reading of the signal-slit, that is, which is the less deviated, corresponds obviously to the smaller refractive index, ω in the case of a positive crystal and ϵ in the case of a negative one ; the more deviated image corresponds to the larger refractive index, ϵ for a positive and ω for a negative crystal. The angle of minimum deviation δ is the only variable, for α the angle of the prism is the same for both. From the formula given in Chapter XXXVII. (page 816) for the calculation of the refractive index μ, namely,

$$\mu = \frac{\sin \frac{\alpha + \delta}{2}}{\sin \frac{\alpha}{2}},$$

it will be clear that the index varies directly as δ, which only occurs in the numerator.

When the first mode of cutting the prism has been adopted, that of Fig. 617, the refracting edge being parallel to the optic axis, the image which is alone visible when the Nicol is at 0° is formed by rays vibrating perpendicularly to the optic axis and to the refracting edge of the prism, and affords ω. The other weaker image seen alone when the Nicol is at 90° is afforded by rays vibrating parallel to the optic axis and to the refracting edge, and therefore gives ϵ.

When the second mode of cutting has been adopted, that of Fig. 618, the 0°-image is formed by rays vibrating parallel to the optic axis, and corresponds to ϵ. The 90°-image on the other hand is afforded by rays vibrating parallel to the refracting edge, as usual for a 90°-image, and also perpendicularly to the principal axis, and gives ω.

In order to arrive at a final result free from all possible slight errors, whether due to the crystal or to the measurements, it is advisable in preparing six prisms of each substance investigated, three on each plan, as above recommended, that the three prisms in each case should be orientated in three different positions about the optic axis, so that the value of ω may be obtained for three different radii of the circular section. By so doing not only is the accuracy enhanced but absolute proof is obtained that the refractive index along different equatorial azimuths is really identical, and that, therefore, the equatorial section of the optical indicatrix is in truth a circular one.

When the crystal is tetragonal two of the three positions should be those of the lateral rectangular axes, and the third one of the 45°-interaxes. When the crystal is hexagonal or trigonal two of the positions should be those of two adjacent 60°-hexagonal axes, and the third one of the 30°-interaxes. The mean of all six results for each index may be confidently taken as the true value. The determination should in every case be made for the usual six wave-lengths of light.

Biaxial Crystals.—If the crystal belong to the rhombic, monoclinic, or triclinic systems it will possess three refractive indices, namely, α the lowest expressing the refraction along the minimum axis of the optical indicatrix, now an ellipsoid of general form having three different rectangular axes, β the intermediate index representing the refraction along that rectangular axis of the optical indicatrix which possesses an intermediate length, and γ the highest refractive index denoting the refraction along the maximum axis of the indicatrix. A 60°-prism, the bisecting plane of which contains two of these three principal axes of the optical ellipsoid, and the refracting edge of which is parallel to one of these two axes, will afford two of the three indices directly. Hence two prisms may be ground which between them will afford all three indices of refraction and one in duplicate. But a complete investigation should include the preparation of six such prisms, two affording α and β, two furnishing β and γ, and two others yielding α and γ. Each index is thus obtained four times, and the mean value may be taken as the truth when the individual values are concordant. When the crystal is rhombic, the directions of the axes of the optical ellipsoid are known from the symmetry. If the crystal be monoclinic, the orientation of the ellipsoid will have been ascertained by determinations of extinction with the aid of section-plates parallel to the symmetry plane. If triclinic, the more difficult determination of the position of the ellipsoid will have been achieved by making a number of extinction observations on a variety of section-plates or tabular crystals, and by the examination of the optic axial interference figures in convergent polarised light.

The preparation of a 60°-prism from a rhombic crystal is especially simple. The zones of faces developed will usually enable the desired principal crystallographic plane, identical with a principal plane of the optical ellipsoid, and which is to be the bisecting plane of the prism, to be adjusted at once, as also the direction of the crystallographic and optical axis which is to be the direction of the refracting edge of the prism. The case of a monoclinic crystal is nearly as simple, the rotation of the optical ellipsoid in the symmetry plane (that is, about the symmetry axis) being the only additional complication, and the setting of this can be readily carried out with the aid of the graduated adjusting movements provided on the cutting-and-grinding goniometer, including the use of the special 60°-prism-preparing adjusting apparatus. The plane of symmetry of the monoclinic crystal can usually be very readily set vertically, parallel to the axis of the goniometer and parallel also to the plane of the prism-cutting 120°-adjusting-segment; it can then be rotated through the extinction angle by means of the upper ordinary adjusting

segment, so as to bring one of the two axes of the optical ellipsoid lying in the symmetry plane vertical, after which both faces of the 60°-prism can at once be ground in succession, without detaching the crystal after the grinding of the first surface, by merely rotating the large segment for 60° first on one side and then on the other side of the adjusted position.

In the case of a triclinic crystal, when once the much more difficult task of discovering the orientation of the optical ellipsoid is achieved, the knowledge can at once be applied and experimentally translated on the cutting-and-grinding goniometer, and the necessary prisms cut or ground almost as readily as for a monoclinic crystal.

The cutting-and-grinding goniometer thus enables the necessary 60°-prisms to be prepared for crystals of every variety of symmetry. It is consequently an invaluable instrument, providing as it does the means of directly determining the primary optical constant, refractive index, with ease and accuracy. It would be waste of time, in the author's opinion, to dilate on other very much less accurate means of obtaining prisms of artificial or mineral crystals. Occasionally prisms of 55°-65° angle are naturally available by the prismatic formation of the crystal itself, a couple of suitable faces of a prominent zone being especially well developed at an angle not too far removed from 60°. When the angle exceeds 65° there is danger of total reflection occurring within the crystal, and non-emergence of the refracted rays. Less than 55° brings down the accuracy somewhat. It is not a very frequent occurrence to find such a pair of faces fortunately placed, in relation to other faces present, as to permit of light passing through in the correct position for minimum deviation, but whenever it does happen, and the faces of the prism are such as yield excellent images of the signal, such a prism may well be used. Every effort should be made, however, to obtain at least the smaller grinding goniometer illustrated in Fig. 705 (p. 942), and if the larger apparatus shown in Fig. 702 (p. 933) can be procured, one is then in the position of being as well prepared for the cutting of the prisms of hard mineral crystals, as for the grinding of those of softer artificial chemical preparations. So fundamental is this constant, refractive index, as regards crystal optics, that the acquirement of one of these instruments is, in the author's opinion, as important as the acquisition of a good goniometer itself.

The actual determination of the refractive indices for a number of different wave-lengths of light is the same in all cases, and a description of the method of carrying it out will now be given.

Measurement of the Angle of the Prism.—This is carried out precisely like the measurement of an ordinary crystal angle, as described in Chapter IV., on the goniometer which is being used as spectrometer, the crystal being mounted, however, with hard optician's wax (softened for the mounting by warming) instead of the usual more pliable goniometer wax, on one of the usual crystal-holders. The adjustment of the crystal-prism for the angular measurement serves also to adjust it for the subsequent determination of minimum deviation. The author always employs the large Fuess No. 1*a* goniometer, described in Chapter XXVI., and shown to the right in Fig. 734, for refractive index determinations, but the ordinary crystal-measuring Fuess goniometer

No. 2*a* serves almost equally well, as shown to the left in Fig. 735. If, on examination of the prism during its adjustment for the measurement of the angle between the two ground and polished surfaces, the latter should be found insufficiently polished to afford a clear refracted spectrum or pair of spectra, and also in all cases of deliquescent or rapidly alterable crystals, the two surfaces may be covered with correspondingly small pieces of microscope cover-glass, selected, after testing their reflections on the goniometer, for true planeness of surface. The selected discs should be cut up carefully with a diamond into the desired small rectangular or other conveniently shaped pieces, and two of them cemented over the refracting surfaces with hard Canada balsam dissolved in benzene. In this case the crystal must be allowed to remain in position on the crystal-holder for at least 24 hours, for the balsam to dry and set hard, after verifying that the glass plates have been properly attached and that the angle is not appreciably altered thereby, and that good refracted images of the signal-slit are now obtained. Provided great care has been taken to select good cover-glasses reflecting perfect single images of the Websky slit, the author has found no error to be introduced by the use of such cover-plates, at any rate not greater than one or possibly two units in the fourth place of decimals of the refractive index, and this is entirely eliminated when the mean of the four values for each index is taken, and is anyhow less than the differences exhibited between the values yielded by different prisms of the same orientation, which often amount to three or four or even more such units. In the great majority of cases, however, an adequate polish will be able to be given to the ground surfaces, by finishing with the polished glass polishing lap, moistened with either a trace of brick oil or, in many cases of artificial salts not very soluble in water, with the moisture of the breath.

Determination of Minimum Deviation.—Having adjusted the crystal-prism and measured its angle in the usual manner with the aid of the white-light goniometer lamp, it is next arranged for minimum deviation. The collimator and the circle being fixed, the telescope is rotated until it is in line with the collimator, and the Websky signal-slit is then directly viewed through the telescope and its image adjusted to the crossed spider-lines. This "direct reading" is then read off on the circle and recorded. The crystal axis and the telescope are next rotated, independently of the circle, until they are in the position for probable minimum deviation, the telescope being some 30° to 40° away from the direct reading and the crystal-prism so arranged that light from the collimator shall be refracted through it parallel to the imaginary third side and base of the prism and enter the telescope, as in Fig. 602 (page 815) in Chapter XXXVII. The image of the Websky slit broadened into a spectrum, or the pair of such spectra if the crystal be other than a cubic one (see Fig. 736), will then be seen on looking through the telescope after a few trials in slightly varying positions of either crystal or telescope, and should then be adjusted absolutely for minimum deviation; when thus adjusted the slightest rotation of the crystal prism in either direction will cause the image or images to move further away from the direct reading.

The whole apparatus as used by the author for the determination of minimum deviation is shown in Fig. 734. It consists essentially of the spectrometer-goniometer, the monochromatic illuminator, and the electric lantern as source of light. Two accessories are left out, for the sake of showing the essential parts more clearly: one is a folding screen of thick cardboard, covered on the outside with dark red cloth and on the inside with black velvet, which surrounds the goniometer on three sides and effectually screens off all stray light from the lantern, the room being otherwise dark; the other is a white-light lamp, an electric (half-watt, thick filament, 120 candle-power) glow lamp surrounded by a brass cylindrical shade, the latter pierced by a window of the same diameter as the collecting lens of the illuminating tube of the goniometer (a continuation of the collimator) and at exactly the same height. This little lamp stands at the right-front corner of the base-board of the spectroscope, together with a switch for it (see Figs. 725, p. 980, and 738, p. 1005, in which it is shown).

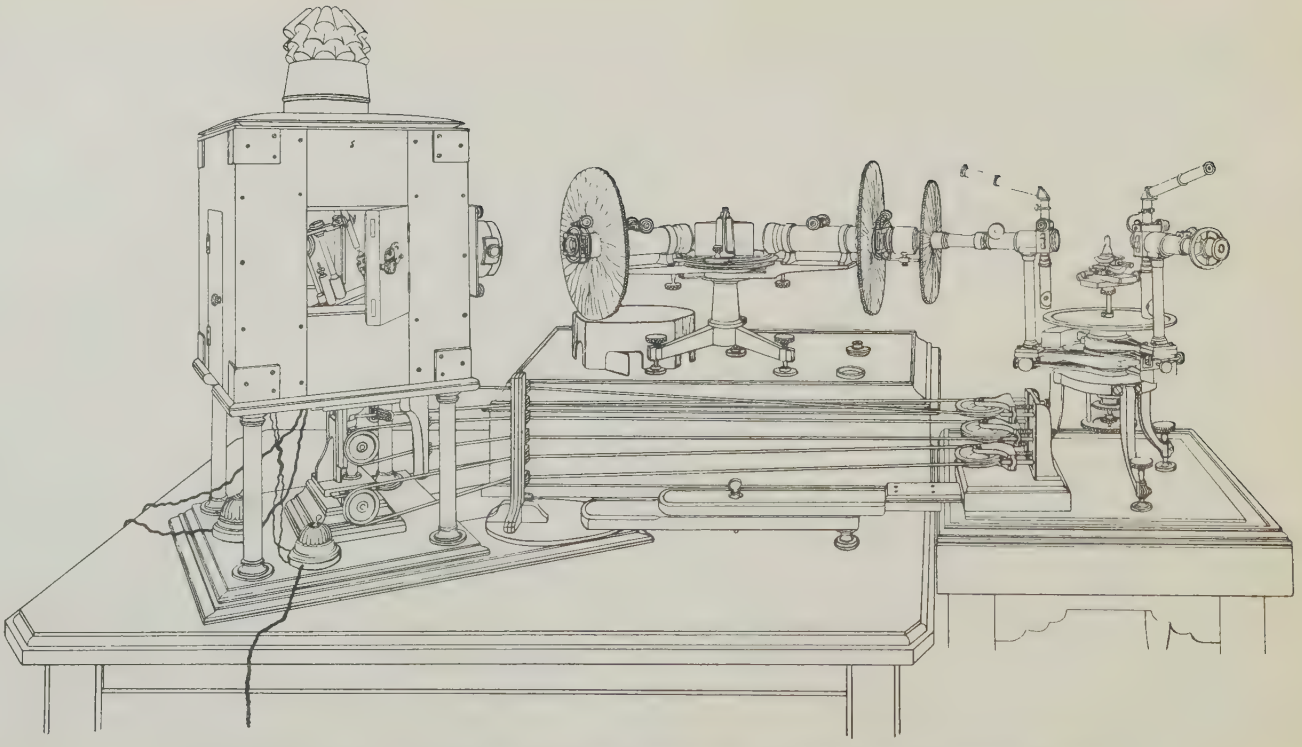


FIG. 734.—The Fuess No. 1*a* Goniometer, the Spectro-monochromatic Illuminator, and the Electric-arc Lantern, arranged for the Determination of Refractive Indices.

It will be observed that the lantern and spectroscope are arranged on a large table in the convenient positions for the illumination of the slit by the converging rays from the lantern condenser, filtered from the heat rays through a circular water cell two

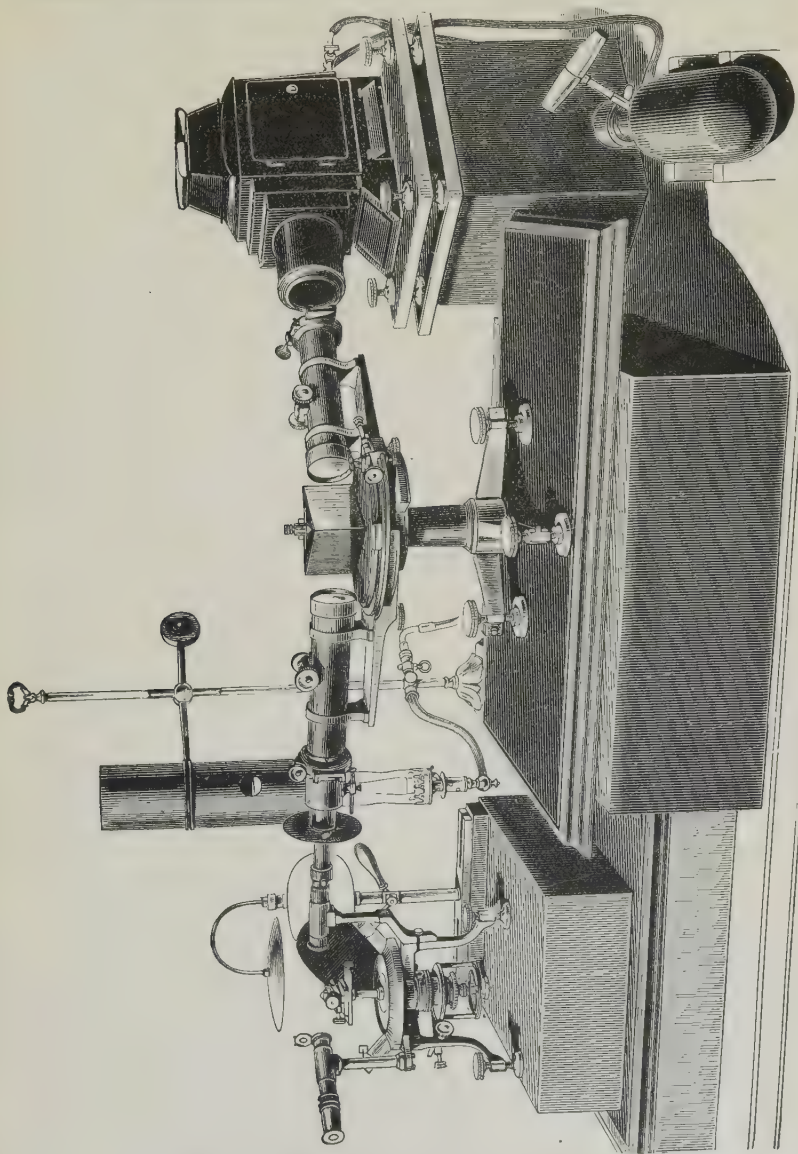


FIG. 735.—The Fuess No. 2*a* Goniometer, Monochromatic Illuminator, and Li.nelight Lantern arranged for Refractive Index Determinations.

inches thick fitting in a short tubular receptacle for it in the lantern front. The spectroscope is arranged to come up to the right-hand edge of the table, to which the goniometer is also brought up, so that the illuminating tube of its collimator may just fit into the diffusing tube in front of the exit slit of the spectroscope. This is a

very convenient mode of working, and particularly so inasmuch as it permits of the very ready use of the pulley-gear adjustment for the lantern arc. It is especially desirable that such a means should be available of absolutely centring the electric arc, for although the Brockie-Pell or Oliver self-feeding electric arc-lamp so nearly maintains a constant position, still in refractive index work it is a great advantage to be able to give it just the last touch of adjustment while actually observing the illuminated images of the Websky slit. This the pulley gear enables the observer to do with his left hand, while his right is free for the goniometer, and the maximum light can be obtained at any critical moment without taking the eye from the telescope of the latter or rising from the observing stool.

Another arrangement, which the author has of late adopted, is shown in Fig. 738, on page 1005, which illustrates the determination of refractive indices at higher temperatures. The lantern is mounted on its usual stand for projection and all other purposes, and the spectroscope also on its own stand, which is the same basal plinth as is shown in Fig. 734, but mounted on a special four-legged pedestal on castors. All the observing instruments in the author's laboratory have now been so mounted on separate stands, all of exactly such a height as brings the optic axis of the instrument to the same level as that of the projection axis of the lantern. Hence at any moment the spectroscope can be brought up to the lantern, and fed with the rays from the electric arc, and any instrument in the room can then be brought up to the diffusing tube of the spectroscope and fed immediately with a stream of monochromatic light.

In Fig. 735 is shown a simple way of determining refractive indices with the No. 2*a* goniometer, and the lime-light as source of light with which to feed the monochromatic illuminator. Very good work is possible even with this arrangement. An incandescent gas mantle is also employed instead of the white-light electric glow lamp, it being assumed that no electric current is available.

Whatever mode of disposition of the three essential parts of the apparatus for determining refractive indices is adopted, the following is the method of work: The finer of the two ground-glass diffusing screens is used in the diffusing tube in front of the exit slit of the spectroscope, to diffuse laterally the monochromatic ribbon of light issuing from the latter, and the condensing lens of the illumination tube forming the prolongation of the collimator of the goniometer is brought almost close up to the ground-glass surface, shaded by the short tube carrying the latter. Even a very small crystal prism, having only faces a square millimetre in area, when perfectly transparent (and no other should ever be selected if possible) yields monochromatic images of the Websky slit of great intensity when the electric arc is the source of light, even although the opening of the exit slit (as well of course as of the entrance slit) is so fine as only to transmit the three-hundredth part of the visible spectrum. The pair of such brilliantly coloured images yielded by a prism of a doubly refractive crystal form magnificent objects in the field of view, changing their colour and their positions as the prism circle of the monochromatic illuminator is rotated so as to permit light of the various wave-lengths in succession to pass through the exit slit. They are shown in Fig. 736, as seen separated at an average distance in the field of the telescope, one of them adjusted to the vertical spider-line for minimum deviation.

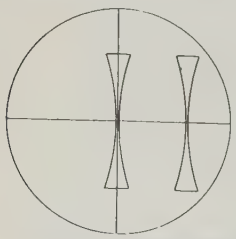


FIG. 736.—The two Images of the Websky Signal-slit afforded by a 60°-Prism of a Doubly Refracting Crystal.

When the double refraction is small, and the two images are consequently close up together, the setting of one of the images to minimum deviation will usually suffice for both; but when the images are fairly widely separated, corresponding to a larger amount of double refraction, the two images require to be set independently for minimum deviation. Hence, it is best to be on the safe side and always to set each

image for each wave-length employed truly to minimum deviation, or to verify the setting if no further adjustment is required. A mere trace of further adjustment is, as a rule, all that is required to make it perfect after the setting has already been achieved for the previous measurement of the position of the other image or for another wave-length.

The process of ascertaining the minimum deviation for the various wave-lengths, say the six already specified as being conveniently spaced (red Li-light, bright red C-hydrogen, yellow Na, green Tl, greenish-blue F-hydrogen, and violet hydrogen near G), is very simple, consisting of five operations.

(1) The prism circle of the monochromatic illuminator is set to the reading for the particular wave-length it is desired to commence with, which may most conveniently be that corresponding to sodium light, as affording the most intensely illuminated images and being more or less centrally situated in the spectrum.

(2) The Nicol prism in front of the eyepiece is set to its 45°-graduation, which permits both images of the Websky signal refracted by the crystal (assuming the latter to belong to one of the doubly refracting systems) to be seen and approximately adjusted; the Nicol is then rotated to its 0°-graduation, its vibration plane being then horizontal, the image corresponding to which has already been pointed out to be slightly more intense of the two images afforded by such a prism. This image, corresponding to light vibrations perpendicular to the refracting edge and in the bisecting plane of the prism, will now be seen at full intensity, while the other, corresponding to vibrations parallel to the edge of the prism and to the 90°-setting of the Nicol, will be extinguished. This 0°-image is then finally perfected as regards its setting to minimum deviation, that is, so that it is symmetrical to both spider-lines of the eyepiece, the vertical spider-line bisecting it longitudinally so that the central very narrow part of the Websky image is practically coincident with the line, a minute amount only of the image being here visible equally on each side, as shown in Fig 736. The slightest rotation either clockwise or anti-clockwise of the crystal axis of the goniometer should cause the image to move away from this setting for minimum deviation, and in the same direction, that of larger deviation, this adjustment of the telescope, and of its spider-line to the image, being the nearest that can be achieved to the direct-reading position. When the adjustment is thus perfect, the circle is read, and the reading recorded as that for minimum deviation for this wave-length and this image, corresponding to vibrations along the known axis of the optical indicatrix. Its difference from the direct reading of the Websky slit, when telescope and collimator were in the same straight line, is the minimum deviation angle required.

(3) The Nicol is next arranged at its 90°-graduation, and similar operations are carried out on the second (slightly fainter) image then transmitted, the vibrations of which are parallel to the refracting edge of the prism, and to that axis of the optical indicatrix parallel to which the edge has been cut.

(4) Leaving this 90°-image adjusted, the circle of the spectroscopic illuminator is then rotated to the graduation corresponding to the next wave-length for which observations are to be made, say red C-hydrogen light, and the image placed at minimum deviation for this, by making use of the fine adjustment of the goniometer telescope, the circle and collimator remaining fixed as all through these determinations of minimum deviation. The amount of fine adjustment given with the telescope of the No. 1*a* goniometer is ample to enable all the images to be brought to the cross-wires by its use, after one has been set to minimum deviation, except in cases of extremely high dispersion and very large difference of the two refractive indices. After also next rotating the Nicol back to its 0°-position and taking the minimum deviation reading of the other image when set to its minimum deviation, the spectroscope circle is again moved on and set for the issue of light of the next wave-length, say Li-light, for which a similar pair of minimum deviation readings are taken. In like manner readings are subsequently taken for the positions of the two images at

minimum deviation for settings of the spectroscope circle for the issue of Tl-light, F-light, and violet hydrogen light. It may also occasionally be desired to supplement these readings by those for other wave-lengths.

(5) At the conclusion of the set of observations of minimum deviation for all the six or more wave-lengths on this side of the direct reading, the telescope is rotated, first to the position of the direct reading itself, the circle being read to confirm and verify this reading, and then to the symmetrical position on the other side of the direct reading; the crystal axis is also correspondingly rotated till the light is incident on that face of the prism which had formerly been the face from which the light had emerged, and a duplicate of the whole series of operations is carried out. The mean of the values of minimum deviation obtained on the two sides of the direct reading, for each of the two images corresponding to the two vibration directions, and for each wave-length of light, is taken as the true angle of minimum deviation for that vibration direction and wave-length, any error of setting to minimum deviation, or in taking the direct reading, being thereby eliminated. There should never be more, at the very most, than three minutes of difference between the corresponding angle of minimum deviation for the same index-image and wave-length for the two sides of the direct reading. In the vast majority of cases the values will be identical, or at most differ by one minute of arc.

The mode of concisely setting down the observations may be best illustrated by the record of an actual determination of the refractive indices of a doubly refracting substance, say of ammonium magnesium sulphate, the substance taken in Chapter XVII. as the example of monoclinic symmetry. On the left-hand page of the note-book the simple record of the observations is conveniently given, and on the right-hand opposite page the corresponding calculations are worked out, in accordance with the formula:

$$\mu = \frac{\sin\frac{\alpha+\delta}{2}}{\sin\frac{\alpha}{2}}.$$

Instead of the general symbol of the refractive index μ, however, the specific symbols of the three refractive indices α, β, γ will of course be given.

Determination of Refractive Indices of Am-Mg Sulphate, $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$. —The prism employed was ground with a refracting angle intended to be 64° (32° each side of the bisecting plane), a favourable angle for this salt. On goniometrical measurement after grinding and polishing on the cutting-and-grinding goniometer the angle actually proved to be 64° 2′. The refracting edge of the prism was parallel to the axis γ of the optical indicatrix, the first median line or acute bisectrix of the optic axial angle. Vibrations parallel to the refractive edge are afforded with the Nicol at 90°.

The other vibration direction was that of the β axis of the indicatrix, the symmetry axis b of the crystal. Vibrations parallel to this direction are transmitted by the Nicol when arranged at its 0°-graduation.

Experimental Data.

Angle of Prism, $\alpha = 64° 2'$. Direct reading of slit : 193° 57'.

Circle Readings for Minimum Deviation.

Light.	Telescope on left of Direct Reading.		Telescope on right of Direct Reading.	
	Nicol at 0° (β).	Nicol at 90° (γ).	Nicol at 0° (β).	Nicol at 90° (γ).
Li	232° 20′·5	232° 53′·5	155° 34′·5	155° 1′·5
C	232 22	232 56	155 32	155 0
Na	232 37	233 10	155 17	154 44
Tl	232 52 ·5	233 25 ·5	155 2 ·5	154 29 ·5
F	233 11	233 42	154 45	154 12
G	233 37	234 10	154 19	153 46

Experimental Data (*continued*).

Angles of Minimum Deviation, δ.

Light.	For Nicol at 0°, β-image.			For Nicol at 90°, γ-image.		
	Left.	Right.	Mean.	Left.	Right.	Mean.
Li	38° 23′·5	38° 22′·5	38° 23′	38° 56′·5	38° 55′·5	38° 56′
C	25	25	25	59	57	58
Na	40	40	40	39 13	39 13	39 13
Tl	55 ·5	54 ·5	55	28 ·5	27 ·5	28
F	39 14	39 12	39 13	45	45	45
G	40	38	39	40 13	40 11	40 12

Calculations.

$\frac{\alpha}{2} = 32° 1'$. Log. sin 32° 1′ $= \bar{1}\cdot72441 = a$.

Light.	For β-index (Nicol at 0°).			For γ-index (Nicol at 90°).		
	$\frac{\alpha+\delta}{2}$.	Log. sin $\frac{\alpha+\delta}{2} = b$.	$b - a =$ Log. β.	$\frac{\alpha+\delta}{2}$.	Log. sin $\frac{\alpha+\delta}{2} = b$.	$b - a =$ Log. γ.
Li	51° 12′·5	$\bar{1}\cdot89178$	$\bar{1}\cdot16737$	51° 29′	$\bar{1}\cdot89344$	$\bar{1}\cdot16903$
C	13 ·5	89188	16747	30	89354	16913
Na	21	89264	16823	37 ·5	89430	16989
Tl	28 ·5	89339	16898	45	89505	17064
F	37 ·5	89430	16989	53 ·5	89589	17148
G	50 ·5	89559	17118	52 7	89722	17281

Results for Refractive Indices β and γ.

Light.	β.	γ.
Li	1·4702	1·4758
C	1·4705	1·4761
Na	1·4731	1·4787
Tl	1·4756	1·4813
F	1·4787	1·4842
G	1·4831	1·4887

A similar series of observations with a second prism, ground to afford α parallel to the refracting edge and β for the other index, yielded the following values, from which will be seen the kind of concordance of the values of the common index, β in the case of this pair of prisms, which may be expected from complementary prisms prepared with the aid of the cutting-and-grinding goniometer:

Values of α and β from Second Prism.

Light.	α.	β.
Li	1·4688	1·4701
C	1·4692	1·4705
Na	1·4719	1·4730
Tl	1·4742	1·4755
F	1·4773	1·4784
G	1·4817	1·4829

The maximum difference between the two values of β for any wave-length is 0·0003, which only occurs once, the differences in four cases being only 0·0001 or nil.

Besides these two prisms four others were also employed, two pairs, each pair yielding all three indices, as in the case of the pair quoted. It will be of interest to give the final values of the three refractive indices derived as the final mean values for all six prisms, from which the relation of the values derived from this one pair to the results of the whole series of observations will be seen.

Refractive Indices of Ammonium Magnesium Sulphate derived from three pairs of Prisms.

Light.	α.	β.	γ.
Li	1·4685	1·4701	1·4756
C	1·4689	1·4705	1·4760
Na	1·4716	1·4730	1·4786
Tl	1·4740	1·4755	1·4811
F	1·4771	1·4786	1·4842
G	1·4814	1·4831	1·4888

The maximum difference of any individual value from the final mean of all is again only 0·0003, which occurs four times. In all other cases it is less, and in seven cases the values are identical. This is a quite typical series of observations, and

indicates how satisfactorily the 60°-prism method works when the prisms are prepared with the aid of the cutting-and-grinding goniometer.

As regards the angle of the prism, 60° is an average convenient size. It will be observed, however, that the angle was 64° in the example quoted. This value, exactly 32° on each side of the bisecting principal plane of the optical ellipsoid, is especially convenient with substances like ammonium magnesium sulphate, of weak double refraction. For the whole spectrum still clearly emerges, and the accuracy is enhanced. On the other hand, in cases of exceptionally high refraction an angle somewhat less than 60° is safer, and as low as 55° is best in extreme cases, owing to the danger with a prism of 60° of the critical angle of total reflection being exceeded in the interior incidence on the second face of the prism, with possibility of non-emergence of at least a part of the spectrum. In cases of very low double refraction the angle may be increased even up to 68° or 70° without such danger. Whatever the angle, however, it must be bisected by a principal plane of the optical ellipsoid, that is, in grinding the prism the crystal must be rotated for an equal amount on each side of that plane in order to grind the two refracting surfaces. These considerations as to the favourable angle must be remembered in deciding as to the possibility of the use of a naturally occurring prism, as already referred to on page 994.

Occasionally, in the cases of rhombic substances the crystals of which are too small for convenient cutting, and of which there are no naturally formed prisms of 50°-70° symmetrical to a principal plane of the ellipsoid, it may happen that a natural prism not exceeding 35° in angle may be formed by two predominating faces on one or more of the crystals, the one a pinakoid face parallel to a principal plane of the ellipsoid and the other a face of a prismatic or domal form also parallel to the same axis of the ellipsoid as the pinakoid face, the refracting edge being thus parallel to that axis. Such a case, shown in Fig. 737, can be utilised for the determination of those two of the three refractive indices the vibrations corresponding to which are parallel to the refracting edge and to the axis of the ellipsoid perpendicular to the latter, lying also in the pinakoid face. The only conditions are that the light shall be incident normally on the pinakoid face and that the refracting edge shall, as usual, be adjusted parallel to the goniometer axis. The prism then behaves as one half of an ordinarily cut 60°-70°-prism, the rays traversing it parallel to the imaginary third side (perpendicular to the pinakoid face) and base. The measured angle of this prism and the measured angle of minimum deviation for any wave-length, will be half of α and δ respectively, as will be clear on comparing Fig. 737 with Fig. 602 (p. 815), and from the obvious facts that the prism angle is half that of the normal case and that the light rays are refracted once instead of twice symmetrically, no refraction occurring at the pinakoid face with normal incidence. Hence to get the α and δ of the ordinary formula we double the measured angles throughout.

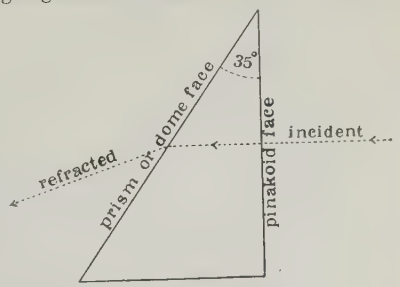


FIG. 737.

To set such a prism with its pinakoid face absolutely normal to the incident rays from the collimator, it is only necessary to set the telescope and collimator at exactly 90° angle with each other (setting them first in line and adjusting as for the direct reading, then rotating the telescope 90°), to adjust to the spider-lines the image of the signal reflected from the pinakoid face, and then to bring the collimator 45° round nearer to the telescope, when its axis will be normal to the face in question. Both collimator and prism must then remain fixed during the observations of minimum deviation.

Determination of Refractive Indices at Higher Temperatures.—This can be carried out very satisfactorily with the No. 1*a* Fuess goniometer and its crystal-heating arrangement described in Chapter XXVI. Full details were given in that chapter of the mode of measuring crystal angles at temperatures up to 200° C. by use of this apparatus, and the measurement of the angle of the prism is carried out in the same manner as that of an ordinary crystal angle. One or two limitations, however, are imposed by the experimental conditions at higher temperatures, compared with the greater goniometrical freedom at the ordinary temperature, when the heating bath and supports are out of the way.

The telescope will usually be arranged to point to that side window of the air bath which is inclined at the smaller angle of 40° to the direct-reading position. For this window permits the refracted images of the signal derived from the prism set to minimum deviation to be viewed by the telescope, while the window at 55°, which is used for ordinary crystal-angle measurements, only does so in the cases of very highly refractive substances. That window which best suits the amount of refraction preliminarily observed to be possessed by the crystalline substance under investigation must obviously be used, and in most cases this will be the one at 40°. The crystal requires to be particularly carefully adjusted on the special movable-button crystal-holder, on which it is gripped either by the two pins or by an improvised clip cut out of platinum foil to suit the shape of the crystal-prism and held between the jaws of the miniature vice carried by the button. The adjustment of the crystal and of the bath, as regards both centring of the crystal within it and the positions of the windows, must be carried out so that both the reflected and refracted images of the Websky signal-slit of the collimator can be viewed equally well through the telescope, and are not cut off by the bath wall adjoining the window. Moreover, it is only convenient to work on one side of the direct reading, there being only one window at 40° and one at 55°, one on each side. Care must be taken also in the centring of the crystal-prism, that the thermometers shall not be touched by the latter or its holder on rotation, as this would upset the adjustment.

With these limitations the process is as described in Chapter XXVI. as regards the measurement of the angle of the prism, and as described in the previous part of this chapter as regards the determination of the angles of minimum deviation for light of the usual six wave-lengths. The whole apparatus as actually arranged during a series of observations is shown in Fig. 738.

It is convenient and saves time to proceed in the following order: The collimator is fixed and its direct reading taken by the telescope, the circle being also fixed. The crystal-prism is then adjusted to minimum deviation at the ordinary temperature, and the telescope rotated round to the necessary position for viewing the refracted images at minimum deviation, and clamped there, so that the middle of the spectrum corresponds to the middle of the range of the fine adjustment. The Nicol in front of the analyser is conveniently arranged at its 45°-position during these preliminary adjustments, so that both refracted images can be seen at once. Before proceeding to

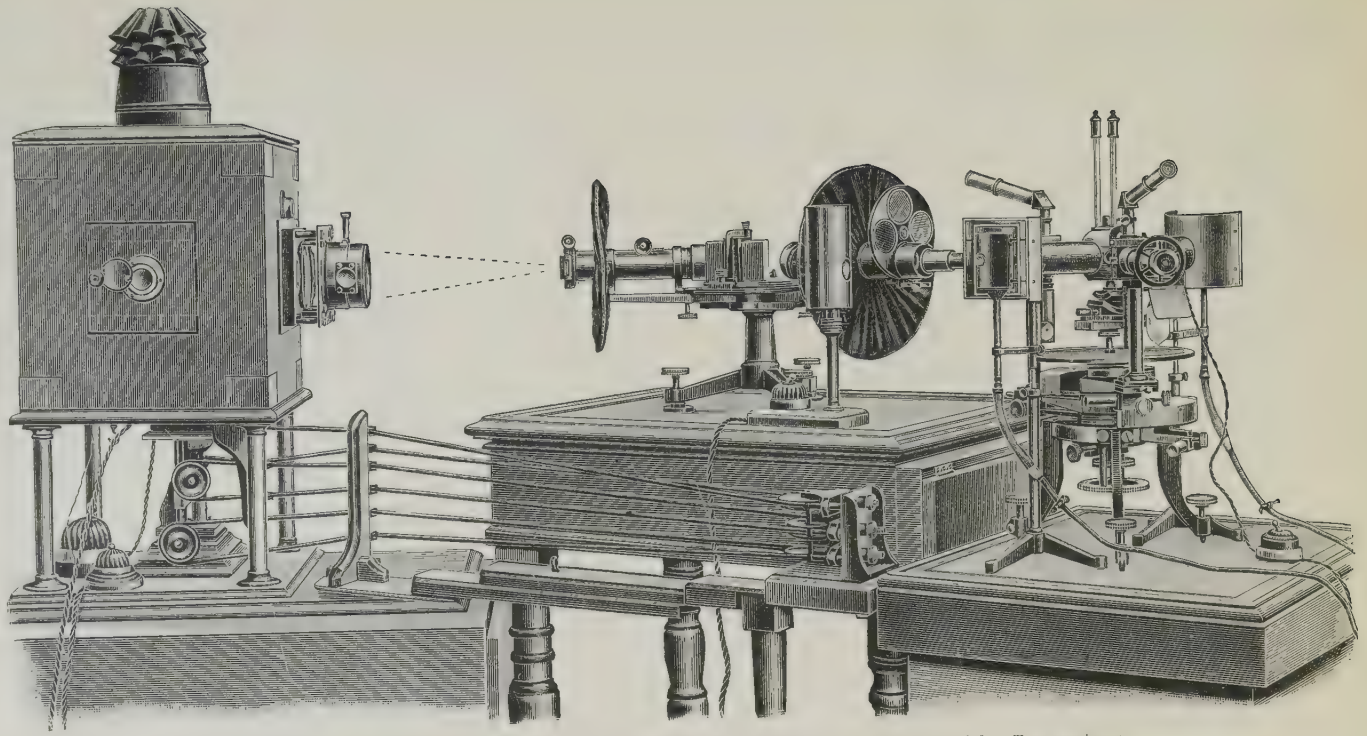


FIG. 738.—Arrangement of Apparatus for the Determination of Refractive Indices at Higher Temperatures.

the measurement of the prism angle the Nicol is arranged at 90°, for which position the reflected light is a maximum, such light as is polarised by reflection from the incident face of the prism vibrating parallel to the refracting edge, and therefore being transmitted by the Nicol when its vibration plane is at 90° ; whereas more or less extinction, complete when the angle of incidence happens to be the polarising angle, of the reflected light occurs when the Nicol is at 0°. When it has been arranged that the two reflected images from the two prism faces, and also the refracted images, are properly visible in the telescope by rotation of the crystal axis, using ordinary white light, the reflected images from the two faces of the prism can be brought and accurately adjusted to the spider-lines and the readings for the angle of the prism taken. For this purpose it is necessary to loosen the circle and fix it to the crystal axis instead. The telescope and collimator are left clamped to the fixed stand and not touched during the measurement of the prism angle. Hence the same value of the circle for the direct reading can be recorded when proceeding to the determination of minimum deviation, and also the telescope is ready at the position for seeing the images at minimum deviation. The whole goniometer and its accessories are then arranged in front of the spectroscopic monochromatic illuminator, as shown in Fig. 738, the illumination tube of the goniometer just entering the diffusing tube of the spectroscope, until the condensing lens nearly touches the ground-glass screen, the finer of the two screens being used.

The circle of the spectroscope is arranged first for the exit of light of the wave-length of the sodium rays, and the images are again reviewed and the measurement of the angle of the prism in sodium light repeated, in order to be quite sure that the adjustments have not been impaired by moving the goniometer. The electric arc should, of course, be regulated with the aid of the pulley gear so that the images are illuminated with their maximum intensity. The prism is then again set for minimum deviation, with the Nicol at first at 45° so as to view both images, supposing the crystal to be a doubly-refracting one ; a couple of measurements of minimum deviation, with sodium light, for each refracted image, with the Nicol at 0° for the one and at 90° for the other (the vibrations being respectively perpendicular and parallel to the refracting edge), may then be carried out, in order to verify that the values for this wave-length for the ordinary temperature, the reading of the thermometer for which is noted, are identical with those already obtained. Greater confidence is hereby imparted to the subsequent comparison of the indices at the ordinary and the higher temperature.

The heating can then be proceeded with, and after constancy at the required temperature has been attained the observations are repeated, as complete a set being taken as possible, beginning with the angle of the prism in sodium light and the angles of the minimum deviation for the same wave-length, and going on to include minimum deviation determinations for the other usual wave-lengths, at any rate for Li-light, C-light, Tl-light, and F-light. G-images are usually too feeble as seen through the glass windows of the bath, owing to the loss by repeated reflection. It is important to finish with a final couple of readings for the positions of the reflected images from the two faces, in order to be assured that the angle of the prism has remained constant during these observations of minimum deviation at the higher temperature. If it has not, another set must be taken, going on if necessary until such is the case. When the precautions for the procuring of constancy of the temperature are taken, which were recommended in Chapter XXVI., the angle of the prism will be found to have remained likewise constant.

Many artificial crystals, those of our example ammonium magnesium sulphate for instance, which contains six molecules of water of crystallisation, will not permit their refractive indices to be determined with

safety at temperatures approaching near 100° C., owing to loss of water and ensuing opacity, unless their ground and polished surfaces are covered with balsam-cemented glass plates, of the miniature kind already described. But it is quite possible to obtain satisfactory determinations with covered faces, provided the very minimum of hard balsam in benzene be employed to cement them on to the faces of the prism, and that it has been allowed to dry and harden for several days before the determination is attempted. Such glass plates do not usually move during an observation at a temperature as high as 80°, although the balsam of course softens, and the fact that the values of the prism angle, obtained before and after the determinations of minimum deviation at this temperature, are identical is a guarantee of no movement. If any movement should occur, the observations must be repeated till none is observed. Such cases of difficulty are usually overcome with patience and a little extra trouble, and satisfactory observations generally obtained even although it may be necessary to re-cement the plates with less balsam (the thinnest possible film being the desideratum) and to wait a few days longer for hardening.

In the case of the prism of ammonium magnesium sulphate affording β and γ, for which the ordinary temperature results were quoted on page 1002, the following results were obtained for the temperature of 70° :

REFRACTIVE INDICES OF AMMONIUM MAGNESIUM SULPHATE AT 70°.

Angle of Prism before Observations of Minimum Deviation, 63° 57′.

Light.	Minimum Deviation Angles.	
	β.	γ.
Li	38° 8′	38° 39′
C	38 10	38 41
Na	38 24	38 56
Tl	38 38	39 11
F	38 56	39 29

Angle of Prism after Observation of Minimum Deviation, 63° 57′.

Light.	Refractive Indices derived from above.	
	β.	γ.
Li	1·4684	1·4737
C	1·4688	1·4741
Na	1·4712	1·4767
Tl	1·4736	1·4792
F	1·4766	1·4823

It will be observed that these values are about 0·002 (ranging from 0·0017 to 0·0021) less than those afforded by the same prism at the ordinary temperature,

as given on page 1002, the usual effect of rise of temperature being to diminish the refraction. The rule is, however, by no means absolute for solids, although it is rigidly valid for liquids and gases. For instance, it was shown by Rudberg and Fizeau that the refractive indices of calcite and certain kinds of glass increase with rise of temperature.[1]

A second prism yielding α and γ gave results for γ practically identical with those afforded by the prism the results for which have just been quoted, while for α the following values were given :

Light.	α.
Li . . .	1·4671
C . . .	1·4675
Na . . .	1·4700
Tl . . .	1·4725
F . . .	1·4757

This example concludes the discussion of the essential details of the practical work on the determination of the refractive indices of a crystal by the prism method.

General Formula for Refractive Index.—The refractive index μ of an isotropic crystal or other transparent substance, or any one of the refractive indices of a doubly refractive crystal, may be expressed for any wave-length λ of the spectrum by the well-known general formula of Cauchy, the theoretical explanation of which has been given on page 819 in Chapter XXXVII. :

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ldots\ldots,$$

in which A, B, and C are constants characteristic of the specific substance. In order to determine them it is necessary to determine μ for three wave-lengths, which may conveniently be red C-hydrogen light, yellow sodium light, and green thallium light; these are three of the six wave-lengths for which it has been recommended in this book that the determinations of the optical constants should always be made. The three values of μ and the three wave-lengths corresponding are then inserted in three equations of condition of the above form, as below, and these equations are subsequently solved for A, B, and C :

$$\mu_1 = A + \frac{B}{\lambda_1^2} + \frac{C}{\lambda_1^4} + \ldots,$$

$$\mu_2 = A + \frac{B}{\lambda_2^2} + \frac{C}{\lambda_2^4} + \ldots,$$

$$\mu_3 = A + \frac{B}{\lambda_3^2} + \frac{C}{\lambda_3^4} + \ldots.$$

The solution of these equations is no light matter, and it may save other workers much valuable time to give here the values of the invariable portions of the calculation, and the simplest possible expressions for the three constants involving these invariables. The expressions

[1] See Ostwald's *Lehrbuch der allgemeinen Chemie*, 1891, vol. i. p. 906.

were found by the method of determinants, and as well as the invariables have been tested times innumerable, and their accuracy proved by the absolute manner in which the refractive indices are reproduced by use of the formula calculated with their aid. The wave-lengths employed were practically identical with those given in the table on page 798.

TABLE OF WAVE-LENGTHS, THEIR SQUARES, AND 4TH-POWER VALUES.

Nature of Light.	λ.	λ^2.	λ^4.
Red Li	6705	44957025	2021134096850625
Red C, Hα, $=\lambda_1$	6562	43059844	1854150165304336
Yellow Na, $=\lambda_2$	5892	34715664	1205177326960896
Green Tl, $=\lambda_3$	5348	28601104	818023350018816
Greenish-blue F, Hβ	4861	23629321	558344810921041
Violet H γ	4340	18835600	354779827360000
Extreme Red A-line	7604	57820816	334315240000000

Solving the three equations in their symbolic form above given, by determinants, A works out to an expression which eventually simplifies to the following, which is a particularly convenient form :

$$A=\frac{\dfrac{\lambda_1^4}{\dfrac{\lambda_1^2-\lambda_2^2}{\lambda_1^2-\lambda_3^2}}}{\mu_1}-\frac{\dfrac{\lambda_2^4}{\dfrac{\lambda_2^2-\lambda_3^2}{\lambda_1^2-\lambda_2^2}}}{\mu_2}+\frac{\dfrac{\lambda_3^4}{\dfrac{\lambda_1^2-\lambda_3^2}{\lambda_2^2-\lambda_3^2}}}{\mu_3}.$$

Calling these three fractions k_1, k_2, and k_3 respectively, we have :

$$A=k_1-k_2+k_3.$$

The two other constants are then very simply expressed as follows :

$$B=-\{k_1(\lambda_2^2+\lambda_3^2)-k_2(\lambda_1^2+\lambda_3^2)+k_3(\lambda_1^2+\lambda_2^2)\},$$
$$C=k_1\lambda_2^2\lambda_3^2-k_2\lambda_1^2\lambda_3^2+k_3\lambda_1^2\lambda_2^2.$$

In these expressions the top halves of k_1, k_2, and k_3 are invariables, and their values are given once for all in the next table. There are also given in the table the sums and the differences of the squares of each pair of wave-lengths, and also their products. With these values taken from the table, the calculation of A, B, and C is merely one of simple arithmetic. Having obtained A, B, and C, they can be checked by calculating the refractive indices for the three wave-lengths used in obtaining them, from the formula, the squares and fourth powers of the wave-lengths being taken from the first table. The indices should be reproduced to the last unit in the fourth place of decimals absolutely, if no arithmetical blunder has been made. The reproductions may also be extended to the refractive indices of the other three wave-lengths experimentally used, and also for wave-length A at the beginning of the spectrum if desired, as was usually done by Gladstone and Dale in their well-known work. The reproduction should occur absolutely for Li-light, that for F-light to within one or two units in the fourth place of decimals, while that for violet hydrogen light near G of the spectrum may be as much out as one unit in the third place, as a further term would be required in the formula to afford the refractive index absolutely for this more distant part of the spectrum.

TABLE OF INVARIABLES.

Required for Calculation of:	1st Term.	2nd Term.	3rd Term.
A . . .	$\frac{\lambda_1^4}{\lambda_1^2-\lambda_2^2}=222208793$ $\lambda_1^2-\lambda_3^2=1445874$	$\frac{\lambda_2^4}{\lambda_2^2-\lambda_3^2}=197099599$ $\lambda_1^2-\lambda_2^2=8344180$	$\frac{\lambda_3^4}{\lambda_1^2-\lambda_3^2}=56576392$ $\lambda_2^2-\lambda_3^2=6114560$
B . . .	$\lambda_2^2+\lambda_3^2=63316768$	$\lambda_1^2+\lambda_3^2=71660948$	$\lambda_1^2+\lambda_2^2=77775508$
C . . .	$\lambda_2^2\lambda_3^2=992906316$	$\lambda_1^2\lambda_3^2=1231559076$	$\lambda_1^2\lambda_2^2=1494851076$

Only significant figures have been included in the table. As the refractive indices μ_1, μ_2, and μ_3 have four places of decimals, k_1, k_2, and k_3 must be likewise worked out to four places of decimals, the numbers of figures in the invariables given being just adequate for this to be done accurately. The result for A will consequently have four decimal places. The invariables given for B are also such that on multiplying by k_1, k_2, or k_3 the result will have four places of decimals. After obtaining the final result for B the decimal places can be struck off, as B is only required to whole numbers. It is usually a six-figure quantity. It must be remembered that the sign of B is negative, so that if the value inside the large bracket works out to be negative, as it usually does, the middle term being larger than the sum of the first and third terms, the actual value of B is positive. As regards C, the invariables given have six fewer figures than correspond to their real value, the six right-hand end figures having been struck off as giving unnecessary labour, for they do not influence the result. Hence, after multiplying the product of two wave-length squares by k_1, k_2, or k_3, which have the usual four decimal places, we require to add two ciphers (6–4) to the end result for C, in order to obtain its real value. It generally has 13 figures, although sometimes only 12, which should be spaced in threes for clearness. Of the 13, the first 5 are alone of significance, and after expressing the fifth to the nearest whole number the rest can be left as ciphers. The sign of C varies.

An example will now be given to render all quite clear. The case of the β refractive indices of monoclinic ammonium zinc sulphate, $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$, will be taken.

The observed refractive indices were: for red C-hydrogen light 1·4904, for yellow sodium light 1·4930, and for green thallium light 1·4957.

If it be desired that the Cauchy formula should represent the true refractive index *in vacuo*, these numbers, as taken from the published table of the refractive indices of the salt,[1] should be corrected to a vacuum before use, the correction being usually +0·0004. For the refractive index of air (for light passing from a vacuum into air) is 1·00029, and the observed refractive indices given by the formula $\mu=-\frac{\sin\frac{\alpha+\delta}{2}}{\sin\frac{\alpha}{2}}$ (p. 816) require to be multiplied by this in order to obtain the refractive index for a vacuum. Now $1{\cdot}4904 \times 1{\cdot}00029 = 1{\cdot}4908$. Hence, +0·0004 being the correction, the three refractive indices actually used were:

$$\mu_1 = 1{\cdot}4908,\ \mu_2 = 1{\cdot}4934,\ \mu_3 = 1{\cdot}4961.$$

Finding the values of k_1, k_2, and k_3 with the help of the table of invariables we have:

$$k_1 = 222208793 \div \frac{1445874}{1{\cdot}4908} = 22{\cdot}9113,$$

[1] *Journ. Chem. Soc.*, 1905, *87*, 1144.

$$k_2 = 197099599 \div \frac{8344180}{1{\cdot}4934} = 35{\cdot}2759,$$

$$k_3 = 56576392 \div \frac{6114560}{1{\cdot}4961} = 13{\cdot}8430.$$

Hence $A = k_1 - k_2 + k_3 = 22{\cdot}9113 - 35{\cdot}2759 + 13{\cdot}8430 = 1{\cdot}4784.$

Proceeding next to find B, using these values of k_1, k_2, and k_3 and the table of invariables we have:

$k_1(\lambda_2^2 + \lambda_3^2) = 22{\cdot}9113 \times 63316768 = 1450669466{\cdot}6784$ (1)
$k_2(\lambda_1^2 + \lambda_3^2) = 35{\cdot}2759 \times 71660948 = 2527904435{\cdot}5532$ (2)
$k_3(\lambda_1^2 + \lambda_2^2) = 13{\cdot}8430 \times 77775508 = 1076646357{\cdot}2440$ (3)

Then $B = -\{(1) - (2) + (3)\} = 588611{\cdot}6308$, or 588612.

Similarly to find C we have:

$k_1\lambda_2^2\lambda_3^2 = 22{\cdot}9113 \times 992906316 = 227487744777708$ (4)
$k_2\lambda_1^2\lambda_3^2 = 35{\cdot}2759 \times 1231559076 = 434443548090684$ (5)
$k_3\lambda_1^2\lambda_2^2 = 13{\cdot}8430 \times 1494851076 = 206932234450680$ (6)

Then $C = (4) - (5) + (6) = -23568862296.$

Adding two ciphers to this result for C, as already explained, and retaining only the first five significant figures, we have for the significant value of the constant C:

$$C = -2\ 356\ 900\ 000\ 000.$$

The general formula expressing the refractive index β of ammonium zinc sulphate for any wave-length λ is thus:

$$\beta = 1{\cdot}4784 + \frac{588\ 612}{\lambda^2} - \frac{2\ 356\ 900\ 000\ 000}{\lambda^4} + \ldots.$$

The proof that this formula is correct is that it reproduces the original refractive indices for C-light, Na-light, and Tl-light, when the squares and fourth powers of those wave-lengths, given in the first table, are inserted, and the constants B and C divided by them. In doing this division only the first four or five figures of the squares and fourth powers are significant and need be used, so that the reproducing calculations are only the work of a minute or two. The reproduced values thus actually calculated by use of the formula are given below:

Light.	Reproduced Values.	Observed Values.
Li	1·4904	1·4904
C	1·4908	1·4908
Na	1·4934	1·4934
Tl	1·4961	1·4961
F	1·4991	1·4994
G	1·5030	1·5040

The only deviations from absolute reproduction are thus observed, as expected when only three terms are used, as the blue end of the spectrum is approached, being 0·0003 for F-light and 0·0010 for violet hydrogen light near G.

It is unnecessary to calculate three separate formulæ for the three refractive indices α, β, and γ of a biaxial crystal, or for the two ω and ϵ of a uniaxial one, one calculation for β sufficing in the former case, and one for the ordinary ray ω in the latter case. It is then only necessary to decrease and increase the constant A by the amount of $\beta - \alpha$ and $\gamma - \beta$ respectively, or to alter it by $\omega \sim \epsilon$, for sodium light in each case, in order to reproduce the other indices practically as well as β or ω. For the difference of dispersion rarely exceeds a few units in the fourth decimal place. Thus, in the case

of our example, the α-indices of ammonium zinc sulphate are reproduced when the constant 1·4784 is diminished by 0·0042, and the γ-indices when it is increased by 0·0064, as absolutely, within 0·0002, as in the case of β.

Determination of the Specific and Molecular Optical Constants.—An investigation of the optical constants of a series of chemical salts such as an isomorphous series, or other definitely related set of compounds, is not complete unless it includes the calculation of the molecular refraction and dispersion, in which besides the refractive index the specific gravity of the crystals is taken into consideration, as well as the molecular weight of the substance. In other words, molecular refraction is the combination of the refractive index and the molecular volume. As two kinds of formulæ are in current use for the expression of these optical constants, those of Lorenz and of Gladstone and Dale, and as both have their special value and usefulness, it is advisable that the calculations should be made by means of both formulæ. It will be adequate, however, as a rule for all practical purposes to give the complete set of Lorenz calculations, and only the molecular refraction for red C-hydrogen light in the case of the Gladstone formula, as this quantity is that which has the special usefulness. The formula of Lorenz was obtained from theoretical and mathematical considerations, based on the electromagnetic theory of light, while the formula of Gladstone was a purely arbitrary one, which was found to express the experimental facts. It is singular that experience has shown that there is little to choose between these formulæ, each having their excellences and their slight drawbacks, but as far as the purpose for which the crystallographer employs them is concerned, to exhibit the optical relationships of related molecules, the drawbacks referred to are inoperative, and so either or, better still, both formulæ may be used, confirming the truth of such relationships by the agreement of their indications.

The **Specific Refraction** according to Gladstone and Dale is the refractive index μ, minus unity, divided by the density d, that is, $\frac{\mu-1}{d}$.

The **Molecular Refraction** is this expression multiplied by the molecular weight M, or $\frac{\mu-1}{d}$M.

The quantity $\mu - 1$ was termed by Gladstone and Dale the "refractive energy" and $\frac{\mu-1}{d}$ the "specific refractive energy."

The specific refraction according to Lorenz is afforded by $\frac{\mu^2-1}{(\mu^2+2)d}$, which represents, in accordance with the electromagnetic theory of light, the relation between the velocity of transmission of light and the density of the medium through which it is propagated. The molecular refraction is this quantity multiplied by the molecular weight of the substance, namely, $\frac{\mu^2-1}{\mu^2+2} \cdot \frac{\mathrm{M}}{d}$.

The **Specific Dispersion** is the difference between the values of the specific refraction for two rays near the two ends of the spectrum, generally C red hydrogen light Hα and the violet hydrogen ray Hγ near G of the spectrum.

The **Molecular Dispersion** is the difference between the values of the molecular refraction for the same two rays.

The mean molecular refraction of the crystal is the mean of the values of the molecular refraction corresponding to all three indices α, β, and γ, taken for the same wave-length of light, in the case of a biaxial crystal, and in the case of a uniaxial crystal it is one-third of the sum of the value for the extraordinary index and twice the value for the ordinary index, that is in the two cases respectively we use $\frac{\alpha+\beta+\gamma}{3}$ and $\frac{2\omega+\epsilon}{3}$.

An example will be given to illustrate clearly the mode in which the results are set forth, taking the case of the same salt, ammonium zinc sulphate, crystallising in the well-known monoclinic series, as was used in the calculation of a general formula for the refraction. In the table the symbol n is used for the refractive index instead of μ, in accordance with the continental practice, as the memoir [1] from which these results are taken was published in both England and Germany.

REFRACTIVE INDICES AND MOLECULAR OPTICAL CONSTANTS OF AMMONIUM ZINC SULPHATE, $(NH_4)_2Zn(SO_4)_2 . 6H_2O$.

Refractive Indices.

Index.	Nature of Light.	Values of Index.
α. Vibrations parallel to 2nd median line.	Li	1·4858
	C	1·4862
	Na	1·4888
	Tl	1·4914
	F	1·4947
	G	1·4992
β. Vibrations parallel to symmetry axis.	Li	1·4900
	C	1·4904
	Na	1·4930
	Tl	1·4957
	F	1·4990
	G	1·5036
γ. Vibrations parallel to 1st median line.	Li	1·4963
	C	1·4967
	Na	1·4994
	Tl	1·5021
	F	1·5056
	G	1·5102

Mean of α, β, and γ for Na light = 1·4937.

[1] *Journ. Chem. Soc.*, 1905, *87*, 1145; *Zeitschr. für Kryst.*, 1905, *41*, 341.

Molecular Optical Constants

		α.	β.	γ.
Axis of optical indicatrix				
Specific refraction, $\frac{n^2-1}{(n^2+2)d}=\pi$	C	0·1487	0·1497	0·1514
	G	0·1520	0·1532	0·1549
Molecular refraction, $\frac{n^2-1}{n^2+2}\cdot\frac{M}{d}=\pi\pi$	C	59·27	59·71	60·36
	G	60·62	61·07	61·74
Specific dispersion, $\pi_G-\pi_C$		0·0033	0·0035	0·0035
Molecular dispersion, $\pi\pi_G-\pi\pi_C$		1·35	1·36	1·38
Molecular refraction, $\frac{n-1}{d}M$	C	100·34	101·21	102·51
	Mean of α, β, and γ,			101·35

The density of the salt at 20° compared with that of water at 4°, which was used in the calculations, was 1·932. The molecular weight employed was 398·72. The molecular volume $\frac{M}{d}$ was consequently 206·38.

If it should be desired to compare the mean molecular refraction of the crystal with the **molecular refraction** of its substance **in the state of solution in water,** a determination which proved very interesting in the cases of the sulphates and selenates of potassium, rubidium, cæsium, and ammonium, it is only necessary to determine both the refractive index and the density for two or three concentrated but not quite saturated solutions of accurately known strength. In the year 1868 Gladstone [1] advanced the generalisation that "the refraction equivalent of a solution is the sum of the refraction equivalents of the solvent and of the substance dissolved," and time has shown that this law is substantially correct, such slight differences as are observed, due to change of state, being sometimes on one side and sometimes on the other.

It may be expressed by the following formula, in which the letter p represents the total amount of solvent and substance, and p_1 and p_2 are the respective percentages of the two substances present.

$$p\left(\frac{\mu-1}{d}\right)=p_1\left(\frac{\mu_1-1}{d_1}\right)+p_2\left(\frac{\mu_2-1}{d_2}\right).$$

It is convenient to consider p as unity, however, and p_1 and p_2 as the proportions of the two constituents expressed as decimals, rather than p as 100 and p_1 and p_2 as actual percentages; it is equivalent to dividing out by 100. The expression on the left-hand side of the equation is then the specific refraction of the solution. The first expression on the right is the unknown required specific refraction of the crystalline substance in the dissolved condition multiplied by p_1 the amount of it present, and the second and last expression is the specific refraction of distilled water multiplied by its proportion p_2. The unknown desired specific refraction of the dissolved substance may be called X; the refractive index of water for C-light as determined by the author and corrected to a vacuum is 1·3321, and its specific gravity at the standard temperature of comparison of 20°, compared with its maximum unit density at 4°, is 0·99824.

[1] *Proc. Roy. Soc.*, 1868, *18*, 49.

Hence, the equation to be solved is as under :

$$\frac{\text{Refractive index of solution} - 1}{\text{Density of solution}} = \text{prop. of salt} \times X + \frac{\text{prop. water} \times 0{\cdot}3321}{0{\cdot}99824}.$$

The practical operations required are (1) to make up the solution by weighing out a quantity of the crystals and dissolving them in such a weighed quantity of water recently distilled as will make a nearly but not quite saturated solution ; (2) to determine the density of the solution thus made, by the pyknometer method with cap described in Chapter XXXII., 10 c.c. being required for this operation ; and (3) to determine the refractive index of another quantity of the solution, using a small hollow prism, with truly worked plate-glass sides as thin as is compatible with rigidity and inclined at 60°, for the purpose. The author employs a small prism of about one cubic centimetre capacity, mounted with hard optician's wax on one of the crystal-holders of the No. 1*a* Fuess goniometer-spectrometer. This prism is also very useful for the determination of the refractive indices of highly refractive immersion liquids.

An example will make the determination and calculation quite clear. It is taken from the latest case investigated by the author, that of **ammonium selenate** $(NH_4)_2SeO_4$, and is one of two determinations made with solutions of different concentrations. Weak solutions must never be employed, as electrolytic dissociation may begin to enter. By exception, the common crystals of this salt are monoclinic, the rhombic form isomorphous with ammonium sulphate never being obtained in the pure state. This has been explained in Chapter XXVIII. and an illustration of a crystal given in Fig. 423 (page 514).

Preparation of Solution : 8·7021 grammes of crystals of the pure salt were dissolved in 9·3513 gr. of water, which corresponds to 48·20 *per cent.* of salt and 51·80 *per cent.* of water.

Density of Solution : The specific gravity of the solution at 20°/4° by the method shown in Fig. 527 (page 628), using one of the 10 c.c. pyknometers, was 1·3627.

Refractive Index of Solution : The observed refractive index for C-light was 1·4073, and the value corrected to a vacuum 1·4077. Hence $\mu - 1 = 0{\cdot}4077$.

We have then the following equation, in which the above data have been inserted :

$$\frac{0{\cdot}4077}{1{\cdot}3627} = 0{\cdot}482X + 0{\cdot}518 \times \frac{0{\cdot}3321}{0{\cdot}99824}.$$

Working this out we obtain as the value of X, the only unknown, $X = 0{\cdot}26319$, which is the specific refraction of the crystals in solution.

In order to get the molecular refraction, MX, where M is the molecular weight of the salt, we multiply the specific refraction thus found by the molecular weight 177·98, and on doing so obtain the value **46·84** for MX, the molecular refraction of ammonium selenate in the condition of solution in water.

A second determination with a somewhat weaker solution, containing 43·88 *per cent.* of the salt, yielded the molecular refraction 46·74, the two results being thus in close agreement. The mean, **46·79**, was accepted as the true value.

It will be instructive in conclusion, in order to afford evidence of the general correctness of Gladstone's law—that the refraction equivalent of a solution is the sum of the refraction equivalents of the substance and solvent, and that such minute changes as accompany

the change of state occur on both sides, the differences between the molecular refraction of the dissolved substance and the mean refraction of its crystals being sometimes in one direction and sometimes in the other—to append the following table of the molecular refractions of the alkali sulphates and selenates for the two conditions. It will be seen that the exceptional monoclinic crystallisation of ammonium selenate does not affect the conclusion in the slightest.

Salt.	Mean Molecular Refraction of Crystals.	Molecular Refraction in Solution.	Difference.
K_2SO_4 . .	32·04	33·21	+1·17
Rb_2SO_4 . .	37·55	38·21	+0·66
$(NH_4)_2SO_4$ . .	38·75	39·43	+0·68
Cs_2SO_4 . .	47·48	47·27	−0·21
K_2SeO_4 . .	38·50	39·65	+1·15
Rb_2SeO_4 . .	44·06	44·63	+0·57
$(NH_4)_2SeO_4$ . .	45·92	46·79	+0·87
Cs_2SeO_4 . .	54·35	54·10	−0·25

The values thus pass, along with increase of the atomic weight of the alkali metal, from a relatively very appreciable positive difference in the case of the potassium salt of each group, to a small negative difference in the case of the cæsium salt, the rubidium salt standing intermediate with a small positive difference. The ammonium salt behaves very similarly to the rubidium salt of the same group, a fact in full agreement with the very near identity of the two salts as regards molecular volume, topic axial ratios, and molecular refraction.

CHAPTER XLVII

DETERMINATION OF THE REFRACTIVE INDEX OF CRYSTALS BY THE METHOD OF TOTAL REFLECTION

The foundation of this method has already been discussed in Chapter XXXVII. It was shown that the limit at which total reflection occurs is so sharp that it can be made to appear as the line of demarcation between a brightly and a feebly illuminated portion of the field of an observing telescope, and thus adjusted to a spider-line. Many forms of total reflectometer have been devised, of more or less efficiency. They are roughly divisible into three types, and the best of each of these will alone be described, namely, (1) those in which a plate of the crystal is simply immersed in a highly refractive liquid, (2) those in which the crystal plate is laid against one of the faces of a prism of highly refractive glass, exclusion of air being secured by a film of a highly refractive liquid, and (3) those in which a cylinder or hemisphere of glass replaces the prism.

The critical angle ϕ corresponding to the limit of total reflection is in all cases measured by means of a divided circle, and the refractive index $\mu = \frac{1}{\sin \phi}$, as shown on page 812.

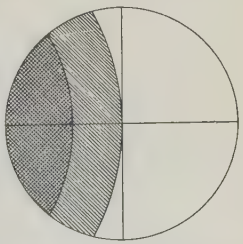


Fig. 739.—The two Limiting Curves of Total Reflection afforded by a Doubly Refractive Crystal.

In the case of doubly refractive crystals there are, of course, two limits, and the two are each duly defined, one after the other, as the boundaries of portions distinguished by differently graded shading in the field of the telescope. A typical field afforded by a doubly refracting crystal-plate is shown in Fig. 739, with one of the limiting curves adjusted to the crossed spider-lines.

(1*a*) **The Kohlrausch Total-reflectometer.** — The simplest of the liquid total-reflectometers is that of Kohlrausch, shown in Fig. 740. A lengthy description of this instrument is unnecessary, as it is now largely superseded by the use of the suspended goniometer of the type shown in Fig. 331 (page 392) in Chapter XXIV., although it has some special conveniences of its own which render it at times a very useful instrument.

The crystal, cemented to a cork plate with gum-arabic, is attached to a somewhat

complicated adjusting apparatus *a*, suspended within a detachable flat-bottomed flask *b*, containing the highly refractive liquid, provided with a plate-glass window *c* opposite the adjustable telescope. A divided circle *d*, with two verniers read by a pair of small microscopes *e*, forms the upper part of the apparatus, and is rotatable above a steel ring *f* carried by the supporting column *g*. A special adjustment *h*, manipulated by the milled head *k*, is provided for the rotation of the crystal in its own plane, which enables the limiting curves to be followed throughout the various azimuths in the plane of the optical ellipsoid parallel to which the crystal has been cut. The adjustable mount for the crystal bears a small graduated circle *l* to record the amount of rotation and identify any particular azimuth, and the cork mount of the crystal is attached to three pins carried by the annulus *m*, pushed into the central boring of the little circle plate. The crystal plate can be adjusted parallel to the rotation axis of the main circle *d* by means of a black-glass mirror *n*, which has been adjusted once for all parallel to that axis. The telescope *o* carries a detachable lens, like a goniometer telescope, for converting it into a low-power microscope with which to view the crystal. Either α-monobromonaphthalene $C_{10}H_7Br$ or methylene iodide CH_2I_2 is employed as the highly

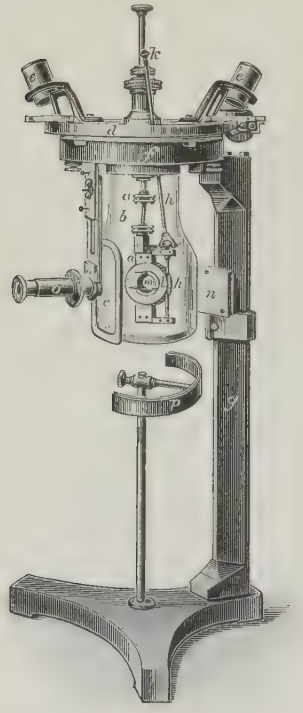


Fig. 740.—Kohlrausch's Total-reflectometer.

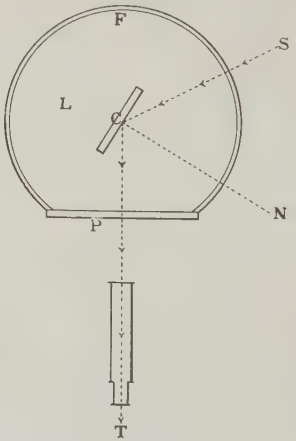


Fig. 741.

refractive liquid, their refractive indices at 20° for sodium light being respectively 1·6657 and 1·7421. When a liquid is required of still higher refraction, sulphur may be dissolved in methylene iodide until the refractive index is raised to 1·85. The observations should be made in a darkened room, and the cork support and any marginal faces of the crystal visible round the plate should be blackened, as the curves are not brilliantly defined with small crystals, and other reflections tend to mask them.

The principle of the method will be clear from Fig. 741, which represents a horizontal section through the apparatus and crystal-plate C. The direction of the normal to the plate is indicated by the dotted line CN, while CT is the direction of the telescope axis, CS is that of the incident light, L is the highly refractive liquid in the flask F, and P is the plane-parallel glass window-plate through which the

observations are made. Diffused sodium or other monochromatic light is allowed to proceed to the crystal along SC from a window, filled with oiled paper, in a blackened cardboard or metal screen, which is fitted round the flask and carried by the semi-circular metallic support *p* in Fig. 740. The monochromatic source of light, usually a sodium flame, is placed near the window, and the crystal rotated until the limiting curve or curves of total reflection are seen and adjusted in the field of the telescope. The latter is conveniently removed at first, so as more readily to locate the limiting curves with the naked eye accommodated for long distance.

(1*b*) **The Suspended Goniometer used as Total-reflectometer.**— With the advent of the suspended goniometer the necessity for the special total-reflectometer just described disappears, although when such a goniometer is not possessed the Kohlrausch apparatus, if available, is, of course, equally efficient. The suspended goniometer of Miers has already been described in Chapter XXIV. and is illustrated in Fig. 331 (page 392), and the simple cylindrical cell with plate-glass front in which the observations are carried out is also shown in Fig. 332. All the necessary adjustments can be given to the crystal-plate, which is suspended in the highly refractive liquid in the cell from the crystal-holder at the base of the adjusting movements. Equally convenient is the author's cutting-and-grinding goniometer described in Chapter XLIII. and illustrated in Fig. 702 (page 933); moreover, in this instrument the adjusting movements are more elaborate and are graduated, enabling any desired orientation of the crystal-plate to be attained with accuracy, with respect to the natural crystal faces left uninjured on the edge of the plate. The cell of liquid is placed on the permanent supporting table of the grinding apparatus, instead of a lap. The cell shown in Fig. 332 is particularly suitable for this purpose, as it carries its own adjusting tripod, for which there is ample room on the grinding table.

A later suspended goniometer devised by Miers especially for refractive index work is shown in Fig. 742, and is a model of convenience and ingenuity. It was constructed by Messrs. Troughton & Simms.

The milled head *a* is the screw for adjusting the height of the crystal-holder. The disc *b* provided with handles, and the milled head *b'*, are for the rotation of the inner cone carrying the crystal-holder, either from above or below, as may be most convenient. The circle *c* is carried by the middle axial cone, and is rotated by the milled head *c'*. A bracket *d*, rotating on the outer fixed cone, carries the telescope *e*, a counterpoise *f*, the verniers *g* for recording the rotation with respect to the circle *c*, a clamping screw *h* and a slow motion for fine adjustment of the relative positions of the circle and telescope, and a clamping screw *k* for fixing the disc *b* to the telescope. The clamping screw *l*, and adjacent fine adjusting screw to its left also marked *l*, adjust the telescope and verniers with respect to the fixed stand and the collimator. The long handles *m* are arranged for convenience of adjusting the circle with respect to the stand while sitting at work in front of the instrument. The milled heads *b'* and *c'* can be clamped together by the fixing screw *n*, which thus locks the disc *b* to the circle *c*. The collimator *o* is fixed to the pedestal column at the back of the apparatus as seen in Fig. 742. The trough for the reception of the highly refractive liquid, or the solution when the instrument is being used for the study of growing faces of a crystal in its mother liquor, may be adjusted for height by the milled head *p*, and fixed at the convenient height by the clamping screw *q*. Three levelling screws *r* are provided for the adjustment of the trough so that the plate-glass window is normal to the telescope

axis. The temperature of the liquid in the cell may be regulated by a stream of water flowing down the outside of the trough from the perforated ring pipe *s*, and carried off by a channel in the adjustable supporting table. A thermometer *t* of suitably bent shape is held by a carrier attached to the bracket *d*, and a stirring arrangement *u* is provided, worked by a motor, the pulley, band, and eccentric gear for ensuring effective stirring by means of the bent glass rod being clearly shown in front and to the left of the figure.

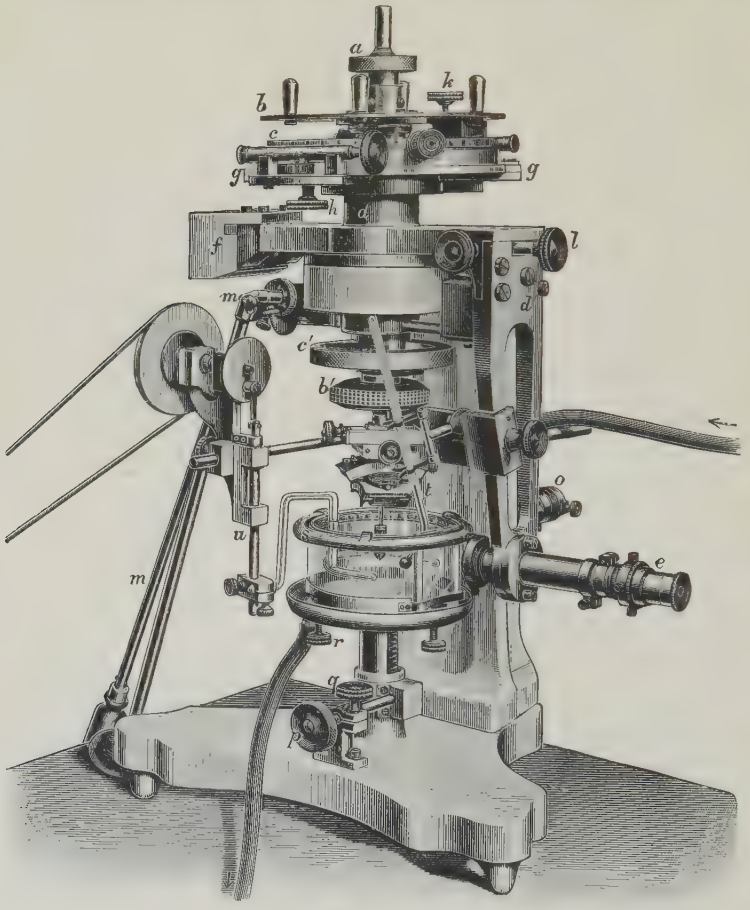


FIG. 742.—Miers Suspended Goniometer-refractometer.

A suspended goniometer is also now constructed by Fuess. To this, or to any form of the Miers suspended goniometer or the cutting-and-grinding goniometer used as refractometer, a direct-vision spectroscope can be fitted if desired, in order to employ the method of Soret, to be described in the next section.

(1*c*) **The Soret Total-reflectometer.** — The method of Kohlrausch [1]

[1] *Ann. der Phys.*, N.F., 1882, *16*, 603.

suffers under the disadvantage that the refractive index of the liquid employed in the cell changes rapidly with variation of temperature. To avoid this serious difficulty, which influences the fourth place of decimals of the refractive index, reversion is generally made to a method employed by Wollaston [1] so long ago as the year 1802, in which a solid prism of known refractive index replaces the liquid. But Soret,[2] who had invented a total-reflectometer on the Kohlrausch principle but with much more elaborate adjustments, in order to eliminate the refractive index of the liquid from his calculations, employed the device of making the determinations in the liquid alternately in quick succession with the crystal and with a prism of known refractive index. If n be the refractive index of the crystal and N that of the prism, and if θ be the

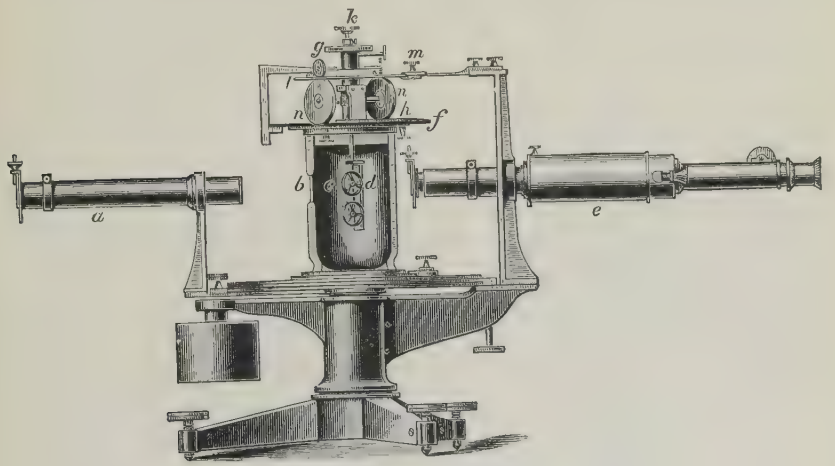


FIG. 743.—The Total-reflectometer of Soret.

limiting angle of total reflection for the crystal and ϕ that for the prism, then

$$n = \mathrm{N} \sin \theta / \sin \phi.$$

With this method of Soret and his identical apparatus some admirable determinations of refractive indices have been carried out by F. L. Perrot,[3] particularly of a number of double sulphates of the monoclinic series $R_2M(SO_4)_2 \cdot 6H_2O$, which have since also been investigated by the author, with the aid of 60°-prisms, by the minimum deviation method. The agreement between the two sets of results is so admirable that it is obvious that this method of Soret, as perfected by Perrot, is capable of enabling very accurate work to be carried out.

The original apparatus of Soret is shown in Fig. 743, and the upper part of the

[1] *Phil. Trans.*, 1802, *92* (2), 381.
[2] *Archives des sciences phys. et nat.*, Geneva, 1883, *9*, 1.
[3] *Archives des sciences phys. et nat.*, Geneva, 1891, *25*, 26 and 669, and 1893, *29*, 3.

apparatus with the later adjusting apparatus of Perrot in Fig. 744. The source of light employed was the sun, the solar rays being directed on the apparatus by means of a heliostat; the refractive indices could thus be determined for the various Fraunhofer lines, those employed by Perrot being *a*, B, C, D, *b*, F, and G. The rays were condensed on the slit of the collimator *a*, and passed through a truly plane plate-glass window at *b* into the liquid cell *c*, in which the object-plate was immersed, being supported at the end of the detachable adjusting and rotating apparatus *d*. After reflection from the crystal the light rays passed out of the cylindrical glass vessel, which with its liquid acted as a cylindrical lens, and were concentrated thereby on the slit of a direct-vision spectroscope *e*. The latter is counterbalanced and adjustable to any azimuth round the axis of the circle and the liquid vessel. The circle-plate *f* carries within its central boring two axes, the outer of which, manipulated by the milled head *g*, is rigidly connected with the vernier *h*, whilst the inner axis, rotated by the head *k*, passes down into the liquid vessel and carries the object-holder *d*. There is an ingenious device for maintaining the reflected rays from the crystal-plate always on the slit of the spectroscope as the angle of incidence is altered. The spectroscope carries with it in its rotation the circular plate *l*, to which it is attached at *m*, and this plate is kept pressed down on two rollers *n*, which rotate over the circle-plate *f* and carry with them both the head *g* and the vernier *h*, so that the latter moves through half the angle of rotation of the spectroscope.

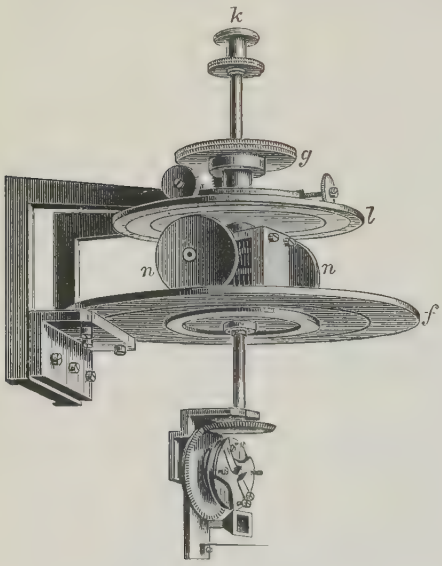


FIG. 744.—Perrot's Adjusting Apparatus for Soret Total-reflectometer.

When the angle of incidence is such that the light is all reflected from the plate the spectrum appears brilliant, but as the angle is diminished the various wave-lengths in succession find their limit of total reflection and become less intense owing to loss of light by reflection. A kind of dark curtain thus traverses the spectrum from one end to the other as the spectroscope is moved, and the more or less sharp edge of this curtain parallel to the Fraunhofer lines is adjusted to such of the latter as it is desired to make determinations of refractive index for. After thus taking a series of readings with the light incident on one side, say the left, the spectroscope is rotated round until the light is similarly and symmetrically incident on the other side, the right, and a second set of readings taken. Half the difference of the two readings for any wave-length is the angle of total reflection required. A similar set of determinations is then carried out with the glass prism of known refractive index, for each of the same Fraunhofer lines, the prism having been previously adjusted with its face parallel to the object-plate. The refractive index of the crystal is then calculated with the aid of the formula given on the last page, which does not involve the variable index of the liquid. Perrot employed carbon bisulphide as the liquid. His method of work was to determine the angle of total reflection for each wave-length with both the crystal and the prism before passing on to the next wave-length, the adjusting holder being merely raised or lowered to bring the one and the other alternately into

line with the spectroscope and collimator. The improved form of adjusting apparatus shown in Fig. 744 was employed, and proved very convenient for this method of procedure.

Probably better work has been done with the above instrument than with any other form of liquid-immersion total-reflectometer, and Perrot's values have proved quite comparable in the fourth decimal place with the author's values for the same crystalline salts, determined by the minimum deviation method with 60°-prisms of the crystals, prepared with the aid of the cutting-and-grinding goniometer. Soret himself determined the refractive indices of a large number of alums, including those containing the rare metals, with his instrument in its original form.

(2) **The Liebisch Total-reflectometer on the Principle of Wollaston.**—The essence of this method is that diffused light is allowed to fall on

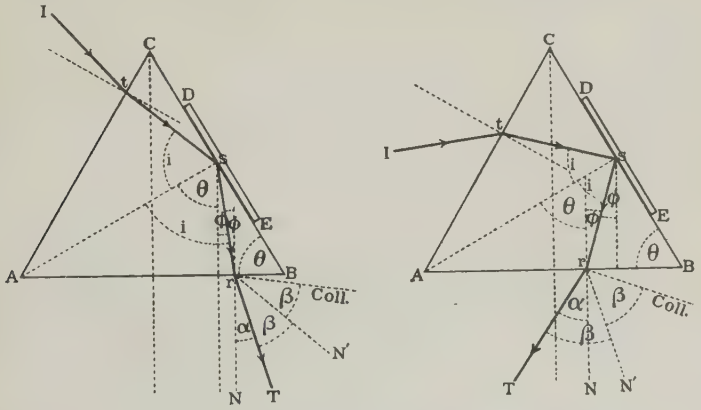


FIG. 745. FIG. 746.

Conditions for the two possible Cases in the Determination of Refractive Index by the Liebisch Total-reflectometer.

one of the faces AC of a 60°-prism ABC of highly refractive glass, as in Figs. 745 and 746, there being two possible cases, in which the light is incident on the face AC to the left (Fig. 745) or right (Fig. 746) of the normal. This face AC of the prism need not be polished, and if left more or less matt-ground itself diffuses the light sufficiently to dispense with the usual screen of oiled paper. The rays then proceed to, and are more or less reflected from, the face BC according to the angle of internal incidence i on BC, and pass out of the prism through the face AB with refraction, ϕ being the internal angle in the prism and α the exterior angle in the air, to a telescope focussed to infinity (for parallel rays), in which the limit between the areas of partial and total reflection is observed. The angle actually observed is α, between the limiting line and the normal to the face AB. The crystal-plate DE, of which the refractive indices are to be determined, is pressed against the face BC, and exclusion of air ensured by a film of a highly refractive liquid, which, being a parallel-surfaced layer of extreme tenuity, does

not affect the result, while avoiding the well-known difficulty of fitting together two polished surfaces without inclusion of air. For even if in the end air be excluded without the use of a liquid film, another difficulty arises, namely, that the two surfaces adhere as if cemented, and it is very difficult to rotate the plate in its own plane (at any rate without scratching the prism face), as is required in total reflection work. Hence, a layer of highly refractive liquid is of great value, not only guaranteeing contact and lubricating the azimuth movement, but also enhancing the transparency and the sharpness of the limiting line or curve.

When the prism is so arranged that the light passing through the first face AC falls on that part of the second surface BC of the prism which is also in common with the crystal-plate, assuming the film of liquid to be infinitely thin, at an angle of incidence less than the critical angle, it is partly reflected and partly transmitted, and the crystal-plate looks darker than the other part of the prism face not covered by it. But on rotating the prism until the critical angle is reached the part touched by the plate looks brighter than the rest of the surface of the prism, owing to all the light striking it being reflected. The actual limit is, as with the liquid method just described, a sharp line or curve clearly visible in the telescope arranged for parallel rays, this being the all-important fact, first pointed out by Abbe, on which the method depends. A highly refractive glass is necessary, its index being higher than that of any crystal likely to be used, and such glass is usually, unfortunately, more or less yellow, and absorbs blue light, and those glasses with the highest refractive index attainable, about 1·96, are also very soft and easily scratched. When, therefore, the refractive index of the crystal is known not to be high, a flint glass prism of 1·64 refractive index can be much more safely employed. The liquid composing the film should, if possible, be of higher refractive index than either the crystal-plate or the prism, but at any rate of higher index than the crystal; α-monobromonaphthalene ($\mu_{Na}=1\cdot6657$) is a very suitable liquid, and in extremely high cases methylene iodide ($\mu_{Na}=1\cdot7421$).

The best form of total-reflectometer based on this principle of Wollaston is due to Liebisch, and is constructed either as a separate instrument, or as a fitting to the Fuess goniometer No. 2*a* in the form of an additional crystal-holder, or again as a larger fitting with more elaborate adjustments, replacing the whole crystal-adjusting apparatus, to the large Fuess goniometer-spectrometer No. 1*a*. As the last is the most efficient it will be here described, although the smaller model works almost as well. It is shown in Fig. 747, in the later form actually used by the author. The prism has an angle of 60° 7′, and its refractive index for sodium light is 1·7781.

A large vertical circle *a*, divided directly on its silver limb into half-degrees, and reading with a pair of verniers *b* to single minutes, is carried in a suitable horizontal axial bearing *cd*. Its axle terminates on the silvered side of the circle in a large milled head *e*, by which the circle, its axis, and a pair of the usual goniometrical crystal-adjusting segments *f* and *g*, are rotated together. The bearing-support *c* is

carried at one end of a bevelled elongated plate *h*, which is rigidly attached below to a slider *i*, moving by rotation of the screw *j* over a fixed dovetailed piece *k* attached rigidly to the circular levelling table *l* which forms the base of the fitting, a boss *m* below the second plate of the table actually screwing to the top of the central crystal-axis *n* of the goniometer No. 1*a*. A second slider *o* moves over the long dovetailed plate *h* at the other end to that on which the circle-bearing is carried, and its sliding motion is brought about by the screw *p*. This slider carries the prism *q* and its means of adjustment, the slider itself effecting the adjustment for approach to the crystal-holder. The 60°-prism has two faces, *r* and *s*, polished plane, but the third face *t* (corresponding to AC in Figs. 745 and 746) is ground to diffuse the incident light. One of the polished faces, *s* (corresponding to BC), is arranged parallel to the circle. The prism is cemented on to a rather tightly fitting little slider *u*, by which the prism

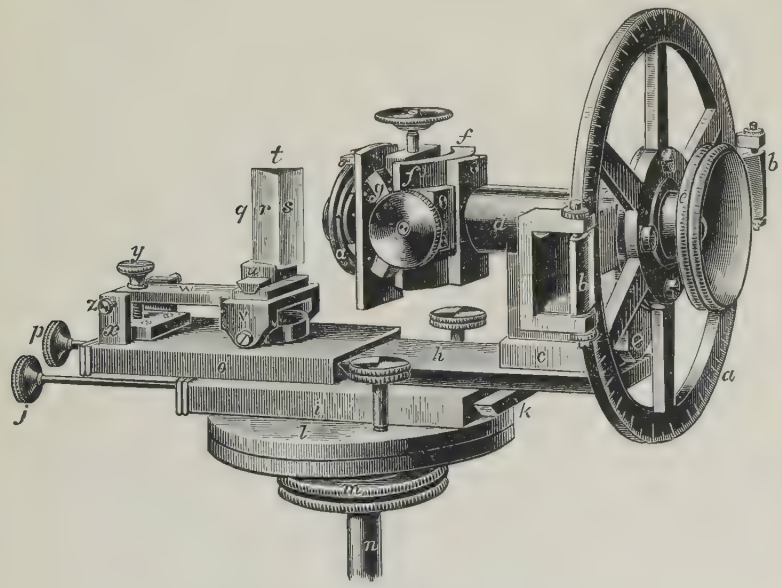


FIG. 747.—The Liebisch Total-reflectometer.

can be moved horizontally parallel to the face *s*. Besides the two horizontal rectangular movements of transference, two rectangular adjusting movements are also provided, one for altitude in the vertical plane and the other for azimuth in the horizontal plane, about two axes parallel to the horizontal and vertical diameters of the circle, which enable the prism face *s* to be set absolutely parallel to the circle if not already so adjusted. They are achieved by mounting the dovetailed bed of the slider carrying the prism on a bracket *v*, which is rotatable about trunnion screws, and by carrying back from the bracket a lever arm *w*, a screw *y* through the outer end of which adjusts the tilt of the face *s* about the trunnion-axis parallel to the horizontal diameter of the circle, a strong spiral spring confined by the screw ensuring the rigidity of the adjustment. The arm is also adjustable for sideways motion, about a vertical axis parallel to the vertical diameter of the circle, by being held within another bracket *x*, in which it is adjustable by the two side-screws *z*, the trunnions of the bracket *v* being attached to a circular disc passing below into a short pin rotatable in the slider *o*. Thus every desirable adjusting movement

is given to the prism, enabling it to be brought up to the crystal in the ideal position.

The crystal-holder is of special construction. The crystal-plate is mounted with optician's wax on a little circular disc which is suspended within a pair of gimbal-rings α, the axes of rotation of which are at right angles to each other, the outer gimbal being hinged from a bracket carried at the top of the basal plate of the holder which carries the fixing peg, a spring pressing this outer gimbal somewhat outwards, so that a little pressure has to be exerted to bring the ring vertical. This pressure is just adequate to ensure good contact between the crystal-plate and the prism when the latter is brought up to the former by manipulation of the screw *p*. The other inner gimbal ensures that the crystal touches the prism equally all over and that the contact remains equal when the circle and the crystal-plate with it is rotated.

The conditions will be rendered clear by Fig. 748, with the aid also of Figs. 745 and 746. The rays I from the source of monochromatic light are allowed to fall on the matt-ground face of the prism *t* (AC in Figs. 745 and 746), by which they are diffused. They then pass in this condition to the second face *s* (BC in Figs. 745 and 746), which is the polished face in contact with the crystal with the intervention of the thin film of liquid. A little screen is arranged between the light source and the prism and quite close to the latter, and the screen is pierced by an aperture of such a size and so arranged that only that part of the surface *s* is illuminated which is common to both crystal and prism. The rays leaving this face, therefore, are only such as are reflected from the crystal-plate; they pass thence to the third face *r* (AB in Figs 745 and 746), also polished, at which they are refracted to the telescope T arranged to receive them, the line R parallel to T (T itself in Figs. 745 and 746) indicating their path diagrammatically. The angle α which the totally reflected rays make with the normal to this exit-face *r*, when the limiting line (or one of the two lines assuming the crystal to be doubly refracting) has been adjusted to the vertical spider-line of the goniometer, is what is actually measured, and it is determined in the following simple manner.

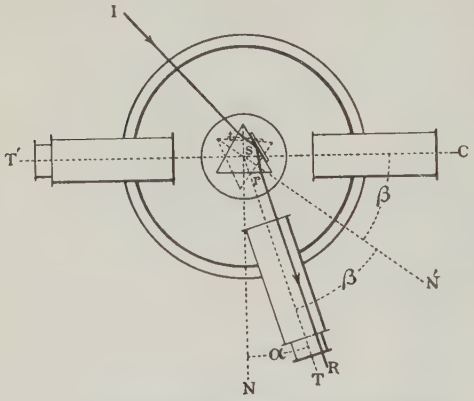


FIG. 748.—Principle of Liebisch Total-reflectometer.

We require first to know the position of the normal to the exit-face *r*, and can find it at once by use of the glass-plate mirror, the Becker fitting shown in Fig. 24 and described on page 41, placed in front of the telescope eyepiece, in order to observe simultaneously the spider-lines and their image reflected from the face *r*. Or, the position of the normal may be found goniometrically as follows.

The collimator C is arranged to the right, about the position shown in Fig. 748, and the telescope T, before being arranged in front, as shown, to receive the rays, is rotated to T′ on the left in order to take the direct reading of the position of the collimator, the total-reflectometer being lowered sufficiently to be out of the way while this is achieved. The telescope is then rotated back to the position T in front which is convenient for the reception of the reflected rays, the total-reflectometer being raised also into position again, and a reading taken for this convenient position of the telescope. The supplement of the difference between the two readings is obviously the angle between the collimator and telescope, an arbitrary but convenient angle which

we may term 2β, so that the half of it, the angle between the lines T and N′ (T*r*N′ in Figs. 745 and 746) is β. The telescope and collimator remaining fixed, the circle is rotated, with the total-reflectometer which it carries, until the limiting line of total reflection is adjusted to the spider-lines of the telescope at T, and a reading is taken. The circle is then further rotated until the Websky signal-slit of the collimator reflected from the exit-face *r* of the prism is also adjusted to the spider-lines, and a reading is taken also for this. The angle rotated through between the two positions is obviously that between the lines N and N′ (in Figs. 745 and 746 it is N*r*N′); for N is the position of the normal to the face *r* when the limiting line is set to the vertical spider-line of the telescope, the angle between N and T (N*r*T) being the angle α which the limit of total reflection makes with this normal N; and N′ is the position of the normal to the same face *r* when the latter has been brought to reflect the collimator signal into the telescope, that is, when the face is equally inclined to collimator and telescope as shown by the dotted prism in Fig. 748, the normal thus bisecting the angle between the two optical tubes. Now this measured angle between N and N′ is clearly $\alpha+\beta$ in the case depicted in Fig. 745, and $\beta-\alpha$ in the case shown in Fig. 746. That is, $\alpha=\mathrm{NN}'-\beta$ in the one case, and $\beta-\mathrm{NN}'$ in the other. As β is known, the angle α of total reflection made with the normal to the exit-face is consequently at once obtained by taking the difference between this measured angle NN′ and β.

Representing now the prism angle between the exit-face *r* (AB) and the face *s* (BC) against which the crystal-plate was pressed by θ, and μ being the refractive index of the glass of the prism, then, as by definition $\mu=\frac{\sin\alpha}{\sin\phi}$, the angle ϕ between the limiting ray inside the prism and the normal N to the face *r* is afforded by the equation $\sin\phi=\frac{\sin\alpha}{\mu}$; and the required angle of internal incidence *i* for total reflection at the face *s* is equal in the two respective cases to the sum and difference of the angle of the prism θ and the internal angle of refraction ϕ, that is, in the case represented in Fig. 745:

$$i=\theta+\phi,$$

and in the case shown in Fig. 746:

$$i=\theta-\phi.$$

These facts should be clear from the two figures, aided by Fig. 748 showing the disposition of the apparatus, the angles being clearly indicated in the two former figures 745 and 746.

(3*a*) **The Pulfrich Total-reflectometer.**—This instrument possesses a highly refractive (more highly refractive than the crystal) glass cylinder instead of a prism, as shown in section in Fig. 749, the general appearance of the instrument being represented in Fig. 750.

From the latter illustration the arrangement of the cylinder, the circle, and the elbow telescope will be obvious. If *l* in Fig. 749 be the limiting ray and μ represent the refractive index of the crystal-plate laid on the plane-polished normal top of the cylinder, μ_1 that of the glass of the cylinder, ϕ the true limiting angle of total reflection within the cylinder, and θ the measured angle at which the limiting ray *l* emerges from the cylinder, then:

$$\sin\phi=\frac{\mu}{\mu_1},\ \text{and}\ \mu=\sqrt{\mu_1{}^2-\sin^2\theta}.$$

If the light enter the cylinder, say, on the left in Fig. 749, the rays *a* and *b* will be partly refracted and transmitted through the crystal-plate

and partly reflected to a and b on the right; while rays c and d, being inclined to the normal (the vertical) at angles greater than the critical angle, will be totally reflected, the limiting line appearing between the two zones at l. The limiting line l is, however, clearest of all when the rays are not incident on the cylindrical surface at all, but on the crystal as at e and f on the top-right of Fig. 749. The incident rays are then partly refracted, e to b and f to a on the left; the rays of grazing incidence (along the direction of the basal plane of the cylinder and under surface of the crystal-plate in contact therewith) will leave the cylinder at the limit of total reflection l; and rays entering on the right below the line of contact of plate and cylinder, say at d and c, will be totally reflected to d and c on the left, leaving the upper part of the field

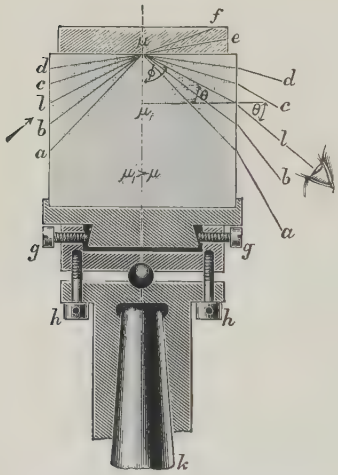


FIG. 749.—Section of Cylinder of Pulfrich Total-reflectometer and its Adjustable Supports.

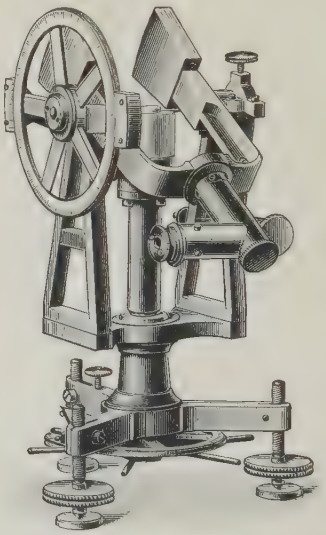


FIG. 750.—The Pulfrich Total-reflectometer.

seen through the telescope quite dark and the limiting line at its maximum sharpness and distinctness. A drop of highly refractive liquid is employed between the plate and the cylinder as usual.

It is a great advantage either with this form of total-reflectometer or with that next to be described in which a hemisphere is employed, to work with a crystal-plate which has been ground circular, and the cylindrical edge-surface polished, as then the light can be readily utilised incident in the manner just described. This, of course, is practically impossible with small crystals of artificial chemical preparations, but when investigations of the refractive indices of minerals occurring in large crystals are concerned it is readily possible. For this reason, moreover, this form of total-reflectometer lends itself readily to class demonstration, especially if the glass cylinder be replaced by one of bromonaphthalene, enclosed in a cylindrical glass vessel, and the crystal-

plate is just immersed in it and sunlight reflected sideways against the cylindrical edge-surface of the crystal-plate.

When doubly refractive crystals are being investigated, the two curves can be followed by rotation of the cylinder and crystal round the vertical axis of the former, and measurement of the total-reflection angle for each curve at a large number of different azimuths carried out. The screws g and h serve to adjust the axis of the cylinder, so as to form

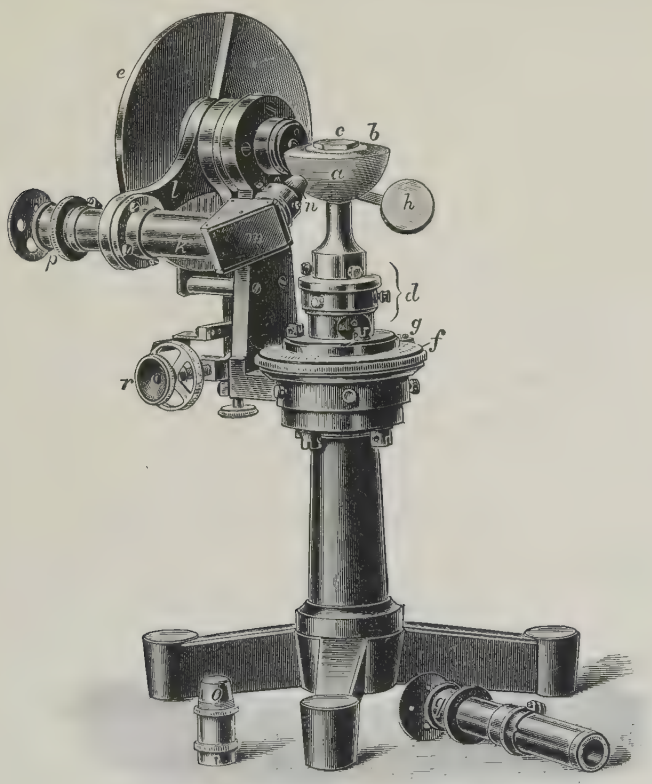


FIG. 751.—The Abbe Total-reflectometer.

precisely a continuation of the inner axis of rotation k of the instrument, and a circle at the end of this axis below the tripod, shown in Fig. 750, enables the azimuth positions to be read off.

(3*b*) **The Abbe Total-reflectometer.**—Bertrand was the first, in the year 1885, to suggest the employment of a hemisphere of dense glass instead of a prism or cylinder. Abbe greatly improved the experimental arrangements, and this form of apparatus has since been perfected by Pulfrich, his successor at Jena, to whose constructive genius we also owe the later form of the total-reflectometer with cylinder just described, the use of a cylinder having been first suggested to succeed the prism of Liebisch by

Abbe. The total-reflectometer with glass hemisphere in its best form as constructed by Zeiss is shown in Fig. 751.

The hemisphere *a* is of Jena flint glass of refractive index for sodium light 1·8904. The method consists in directly measuring the angle of total reflection at the plane surface *b* of the hemisphere, on which the crystal-plate *c* is laid, with a thin film of highly refractive liquid intervening of refractive index at least higher than that of the crystal and preferably higher also than that of the hemisphere, in order to avoid any chance of total reflection before the glass surface is reached. The hemisphere is adjustable by the arrangment *d*, so that its axis of rotation, normal to the plane face of the hemisphere *b*, and that of the divided circle *e*, intersect each other at exactly right angles in the centre of the sphere of which the hemisphere is half. This adjustable support for the hemisphere rests on a second smaller divided circle *f*, the fixed vernier *g* of which is so arranged that its zero mark lies in the plane of the incident light. The large vertical circle *e* is for the measurement of the angle of total reflection, and carries two verniers to right and left, so that the angle can be read on either side of the hemisphere. A mirror *h* serves to illuminate the common face of the crystal and hemisphere, either from below or from above. The telescope *k*, which rotates with a radial arm *l* about the axis of the circle *e*, is arranged elbow-wise, the two parts being connected by a reflecting prism *m*, and the objective fitting *n* is given in duplicate, to suit larger and smaller crystal-plates, the alternative one *o* to that shown in position lying in the foreground. The lens of this fitting forms along with the hemisphere the objective of a telescope arranged for parallel rays, and magnifying two to three times in the case of one of the alternative fittings, while the other fitting reduces the apparent size of the object to about the same extent as the first magnifies. Each corresponds to a separate eyepiece, one *p* being shown in position, and the other *q* lying in the foreground to the right of the alternative objective in Fig. 751. Another lens can be attached in front of the eyepiece to convert the telescope into a low-power microscope, in which the crystal can be viewed when the telescope is rotated over it, and the plate may thus be centred and orientated as regards azimuth with respect to any existing edge-face and the spider-lines of the eyepiece.

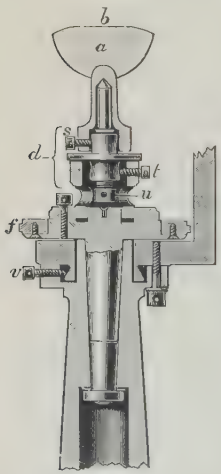


FIG. 752.—Section of the Hemisphere and its Adjustments.

Sodium light is used with small crystal-plates, but if larger plates are available sunlight may be used and the refractive indices determined for the chief Fraunhofer lines. In this case a direct-vision spectroscope eyepiece is employed instead of the ordinary eyepiece *p* or *q*. The fine adjustment of the telescope, during the placing of the limiting curve or line of total reflection to the spider-lines, is carried out by a micrometer screw *r* with divided drum.

As the plane top of the hemisphere, the central part *b* (the outer part of the top being slightly curved and ground matt), becomes more or less scratched with use, owing to the inevitable softness of highly refractive flint glass, a means of polishing it is given, without the necessity for removal from its position and the remaking of the very troublesome centring adjustments. A groove is cut in the cylindrical boss which rests on the circle *f*, for the reception of the band from a whirling apparatus or motor, and when the hemisphere is thus in rapid rotation it may be repolished with a polisher's tool, a disc with handle and covered with soft leather, with the aid of the finest rouge. In case it should, however, be necessary to readjust the hemisphere, the nature of the adjusting movements will be clear from the section given in Fig. 752. The screws *s* and *t* enable the axis of the hemisphere to

be adjusted exactly coincident with that of the circle. The capstan-nut u engaging with the screw thread on the lower end of the fitting which carries the hemisphere affords the means of raising or lowering the latter. Four screws, of which one is shown at v, finally enable the axis of the hemisphere to be made coincident with the goniometrical axis of the telescope.

With all these forms of total-reflectometer the limiting line or curve of total reflection is much sharper when the incidence is "grazing," as already explained in connection with the Pulfrich instrument with cylinder and illustrated in Fig. 749. In the case of this particular form with hemisphere, in ordinary incidence from below, the common surface of the crystal and hemisphere is illuminated from below by means of the mirror, h in Fig. 751, through the hemisphere, and the limiting line found by the telescope and adjusted to the spider-lines, the angle of total reflection ϕ being that made with the normal to the plate and surface of hemisphere. The experiment should be made from either side and the mean of the two values of ϕ taken. According to the other preferable method of grazing incidence the incident rays are caused to arrive from the mirror at a very small angle downwards from above the crystal, passing through its edge-face, which again renders it obvious how advantageous it is, if possible, to have the crystal provided with a ground normal cylindrical edge, although it is at the same time a disadvantage not to have actual crystal faces visible on the edge for azimuth reference purposes. When the rays are thus directed slightly down on the crystal the distinctness of the limit is very marked, corresponding to the refraction of rays parallel to the grazing line along the surface of the hemisphere.

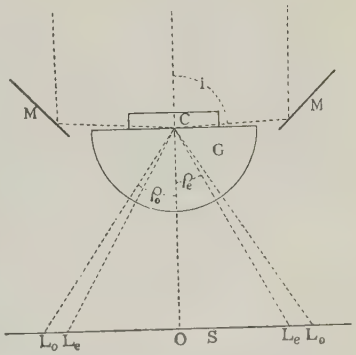


FIG. 753.—Arrangement for Projection and Photography of Limiting Curves of Total Reflection.

Projection and Photography of the Limiting Curves. — This latter method of working with the rays directed slightly downwards is illustrated in Fig. 753. The figure also serves to illustrate the fact that with the glass-hemisphere total-reflectometer it is possible both to project on a screen, and to photograph, the limiting curves of total reflection. That this is practicable was first shown by C. Leiss, following up a suggestion of Pulfrich. It is facilitated, although the addition is not indispensable, by the use of a continuous conical reflector M instead of the ordinary mirror. The crystal C, in Fig. 753, should be a fairly thick plate with cylindrical periphery, and preferably of calcite for demonstration purposes, as the double-curve then consists of a circle and an ellipse, which are rendered objectively visible and clearly separated owing to the large amount of double refraction, as shown in Fig. 754, which represents the photographed projection.

Light is caused to enter by reflection from the conical mirror, from all sides almost horizontally (grazing incidence, the angle of incidence i being nearly 90°) in the margin of the circularly cut crystal plate C, and the rays are received as they emerge from the glass hemisphere G on a horizontal screen S laid under the latter, as shown in Fig. 753. The two pairs of points L_oL_o and L_eL_e indicate where the plane S intersects the two cones of rays corresponding to the two (ordinary and extraordinary) limiting surfaces, and are points on the two section-curves respectively; in the case of calcite these are a circle and an ellipse, the crystal plate being cut and arranged so that the crystal-optic-axis is perpendicular to the plane of the paper.

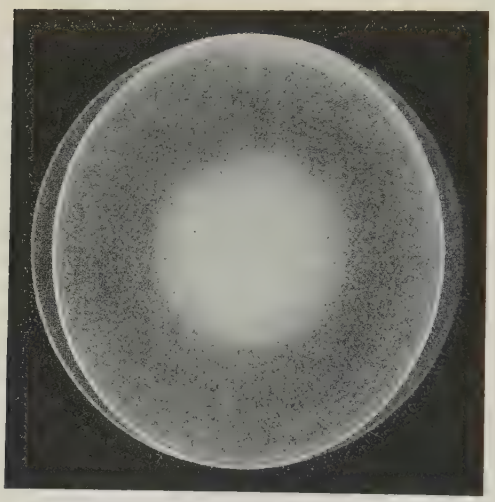


FIG. 754.—Photograph by Wülfing of Limiting Curves of Calcite.

The limiting curve or curves projected on the screen (in general two closed curves) were supposed by Leiss to represent the section-curves of the index-surface of MacCullagh with the surface of the crystal. This, however, is not so, for it was shown by Pockels[1] that its radii vectores are proportional to the tangent of the limiting angle of refraction, instead of the sine of that angle. In the case of a uniaxial crystal, such as calcite, where the index-surface is composed of a sphere and a rotation ellipsoid, the section-curves would obviously be a circle and an ellipse having the relations corresponding to those two portions of the index-surface. If in Fig. 753 ρ_o and ρ_e represent the angles of the two cones corresponding to the ordinary and extraordinary rays respectively, the intercepts of which L_o and L_e on the screen S are points on the circle and ellipse respectively, and if Leiss were correct, the relationship would be that of the sines, as ω to ϵ, namely:

$$\frac{\sin \rho_o}{\sin \rho_e} = \frac{\omega}{\epsilon} = \frac{1{\cdot}6583}{1{\cdot}4864}.$$

Wülfing,[2] however, who has carried the matter further, has shown that the actual relationship, as measured on the photographs, is as the tangents, namely:

$$\frac{\tan \rho_o}{\tan \rho_e} = \frac{\tan 57^\circ 40'}{\tan 49^\circ 14'} = \frac{1{\cdot}580}{1{\cdot}160} = \frac{1{\cdot}6583}{1{\cdot}2176}.$$

[1] *Lehrbuch der Kristalloptik*, p. 110.
[2] *Sitzungsber. der Heidelberger Akad. der Wiss.*, A, 1912, *19*, 6.

The double refraction, as indicated by the figure, would thus appear to be 0·4407 instead of the true value of $\omega - \epsilon$, namely, 0·1719, that is, $2\frac{1}{2}$ times greater than it really is. The curve of the ordinary wave-normals is a circle, the radius of which at the section-plane S is OL_o; that of the extraordinary wave-normals is an ellipse, with semi-major axis perpendicular to the paper (parallel to the optic axis of the calcite crystal) and equal to OL_o also, while its semi-minor axis is represented in direction and length by OL_e.

Thus we obtain by direct projection out of the glass hemisphere, on a plane, limiting curves of total reflection consisting of a circle and an ellipse corresponding, with some exaggeration of the amount of double refraction, to the section-curves of the index-surface. In order to obtain the curves sharp and clear the bundle of incident rays must be narrow, as the focus of the figures lies on a sphere and not on a plane. This can be proved, and excellent sharp figures produced, by fitting over the hemisphere a

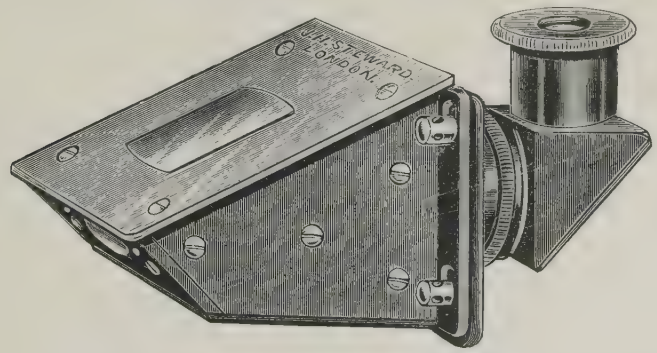


FIG. 755.—The Herbert Smith Refractometer.

larger hemispherical cup of ground glass, of radius corresponding to that of the focal sphere, which was 35 mm. for Wülfing's instrument. The orthogonal projection of this image on the focal sphere, in the direction of the vertical axis, represents truly the two components of the index-surface, namely, the circle and the ellipse, exactly corresponding in their dimensional relations to the correct double refraction, and the actual photograph shown in Fig. 754, which was taken by Wülfing, is that of this projection. Measurements showed that the diameters of the ellipse on the negative itself were 59·9 and 66·3 mm., the theoretical being as 59·4 to 66·3, a fairly close agreement considering all the difficulties of such photography.

(3*c*) **The Herbert Smith Refractometer.**—An ingenious little instrument, shown in Fig. 755, has been devised by Herbert Smith [1] for the rapid approximate determination of the refractive index of a crystal, a gem-stone for instance, and in which at the same time compensation for the spherical curvature of the focal plane has been effected.

This latter is also achieved in the Pulfrich total-reflectometer by the introduction

[1] *Mineralogical Magazine*, 1907, *14*, 354.

of a corrective lens before the achromatic objective. The field of view of the Herbert Smith refractometer is quite aplanatic for its entire range of refractive index, 1·300 to 1·800.

A hemisphere of dense glass is employed as in the Abbe-Pulfrich instrument, and by means of a reference scale, shown separately in Fig. 756, the refractive index may be read off directly to the second place of decimals, and by estimation as far as an approximation to the third. The hemisphere is a centimetre in diameter and of refractive index 1·8049. A convex lens of crown glass of 25 millimetres focal length is arranged with the surface of greater curvature nearest the hemisphere, which enables the spherical focal surface of totally reflected rays to be brought to a plane focus, so that the edges separating the light and dark fields are sharply defined throughout the whole effective range of the instrument. The plane surface of the hemisphere is arranged to be parallel with and to project slightly above the inclined surface-plate of the instrument, the angle between the normal to this plane and the axis of the tube of the instrument being 61°.

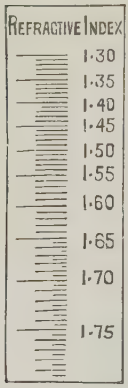


Fig. 756. — Reference Scale of Refractive Indices.

The centre of the field thus corresponds to a refractive index of 1·61. The corrective lens is carried in a vertical sliding frame, adjustable by means of a screw (below, not visible in Fig. 755) for its vertical position. The reference scale, photographed on a glass plate, is carried in a short inner tube, sliding in an outer tube carried by a second vertical frame close to the first one, in near proximity to the corrective lens; it is also adjustable by means of slots and four screws provided with capstan holes, two of which are shown in Fig. 755 proceeding from the front edge of the frame. A positive eyepiece magnifying ten times slides in the outer end of the inner tube, and between its two lenses a totally reflecting prism is mounted, the tube being thus made elbow-shaped instead of straight, so that the eye may be more conveniently placed during the observations. Light is admitted to the instrument by means of a lens of 25 millimetres focus fitted in the back face of the box, which is also inclined at 61°.

The effective range of the instrument is from 1·40 to 1·80 of refractive index. Each interval on the scale corresponds to a difference of index of 0·005 in the higher indices and 0·01 in the lower. In sodium light the limiting line of total reflection separating the light and dark fields is adequately sharp to enable tenths of divisions to be approximately estimated, and this light is used in making the scale with a few substances of known refractive index, so that the scale readings are actual refractive indices.

Even in white light, owing to the violet end of the spectrum being in shadow, the yellow of the spectrum produced instead of a limiting line is sharp enough to enable determinations to the second place of decimals to be made. A sheet of white paper laid on the table is an excellent source of white light. The width of the spectrum seen affords a measure of the amount of dispersion possessed by the substance, and is in itself a valuable indication. For such spectrum width depends on the difference of the dispersion of the crystal and of the glass of the lens; so that a substance of high dispersion, similar to that of the lens, shows an almost colourless limiting line of total reflection, while a substance of low dispersion shows a broad spectrum instead of a sharp line.

Small fragments of crystals only a millimetre in diameter may be used with this instrument, and there is practically no upper limit to the size of crystal or gem-stone which can be tested with the apparatus, the surface plate being itself of some size and its plane clearing all the other parts of the instrument. As only one plane surface is required on a crystal for use with the method of total reflection, a small facet of a gem-stone serves as well as the large table facet of the stone, except that there is more difficulty in being sure of true contact and of not scratching the somewhat soft plane surface of the hemisphere. The upper limit being 1·80, the instrument includes the ruby and sapphire and other forms of corundum within its range. It is constructed by J. H. Steward, Strand.

Hutchinson Universal Apparatus. — A Universal Apparatus was described in January 1911 to the Mineralogical Society by Dr. A. Hutchinson, which is well adapted for the measurement and optical examination of small crystals, and serves as an excellent total reflectometer. It is shown in Fig. 757.

The instrument is a goniometer of the suspended type, mounted on a solid base-plate P, to which a telescope A, a microscope B, and a collimator C, can be clamped in the manner shown at K. The circle D, provided with fine adjustment and fixing screw E, is carried by a rigid column S. The crystal is suspended below the usual adjusting and centring apparatus G, and the inner axis carrying the latter may be fixed at any height by the screw F. The microscope is so arranged that its axis bisects the angle between the optical axes of the collimator and telescope. A cap carrying a Nicol N may be attached in front of its eyepiece, and it is fitted with a Bertrand lens L. The latter, when used with a ½-inch objective, converts the microscope into a diminishing telescope, with which the images of the collimator signal reflected by minute faces can be observed. Another fitting, not shown in the figure, carries a Nicol and a converging lens. When this is placed opposite the objective of the microscope, the optic axial angle of a biaxial crystal can be measured. Further, since any face of the crystal must be perpendicular to the microscope axis, when the image of the collimator signal reflected by the face is seen on the cross-wires of the telescope, a means is afforded of finding the angle at which an axis emerges from a face without employing auto-collimation. Similarly, the plane face of the tank T can be rapidly adjusted perpendicular to the microscope axis by the three levelling screws of the table H, and the instrument then becomes a Kohlrausch total-reflectometer, with which the limits produced by very small faces can be readily distinguished.

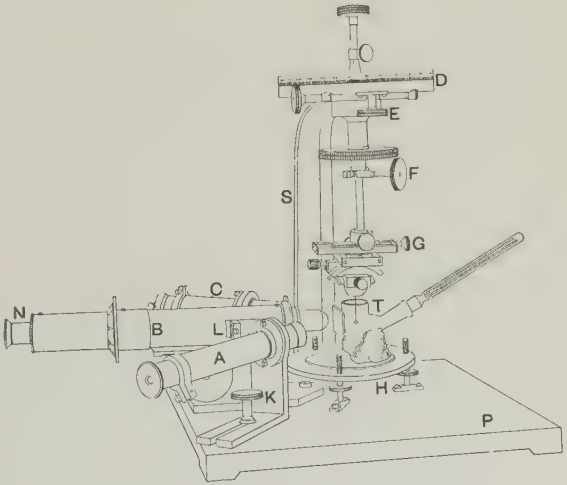


FIG. 757.—The Hutchinson Universal Apparatus.

CHAPTER XLVIII

THE DETERMINATION OF THE OPTIC AXIAL ANGLE AND DISPERSION OF THE MEDIAN LINES

The optic axes of a biaxial crystal are, as already stated in Chapter XLII., experimentally indicated by the positions of the vertices of the two hyperbolic brushes of the interference figure afforded in convergent polarised light by a plate perpendicular to the acute bisectrix of the optic axial angle, when the two Nicols are crossed and arranged at 45° to the plane of the two optic axes. The acute bisectrix is either the maximum or the minimum axis of the optical indicatrix (or *vice versa* for the Fresnel optical ellipsoid) according as the crystal is one of positive or one of negative double refraction. The obtuse bisectrix will be the converse, either the minimum or the maximum axis of the indicatrix. As the crystal-plate is rotated the hyperbolic brushes rotate about their vertices, until when the line joining the optic axes is parallel to the plane of polarisation of either of the Nicols the brushes unite to form a rectangular cross, one arm of which passes through both axes and the other crosses this at right angles midway between the two optic axes, the rings around the latter remaining more or less the same, as described in detail in Chapter XLII. and illustrated by photographs.

If, therefore, the section-plate be adjusted to the first-mentioned position, when the optic axial brushes are opened to their fullest extent, the line joining the optic axes being inclined 45° to the planes of polarisation of the two Nicols, as shown in Figs. 677, 687, and 698 on the Plates IV. and V., facing pages 920 and 926 in Chapter XLII., and the plate is rotated about the diameter at right angles to this line joining the optic axes, first one and then the other of the vertices (the vertex being fortunately the sharpest part of the whole hyperbola in each case) may be brought to the spider-lines of the eyepiece of the polariscope in turn, as shown in Fig. 758, and the angle between these two positions read off on a divided circle carried by the instrument normally to the rotating axis and concentric with it.

The optic axes thus indicated by the hyperbolic vertices are, in all ordinary cases, both the primary and the secondary optic axes, the distinction between which was made clear in Chapter XLI. (pages 881 and 883). For the angle between a primary and a secondary optic axis is usually

so small that the hyperbolic vertex overlaps both, even when the crystal section-plate is so relatively thick as to give very small rings around, and a very sharp brush-vertex at, each optic axis. Hence, for all the usual practical purposes primary and secondary optic axes are identical.

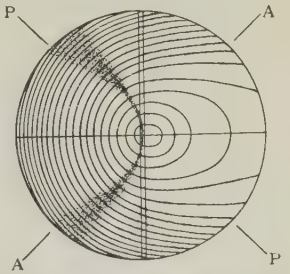


FIG. 758.—Optic Axial "Brush" Vertex adjusted to Spider-lines of Polariscope.

The angle thus measured by the rotation from one to the other vertex is not, however, the true optic axial angle within the crystal, generally symbolised by $2V_a$, but only the apparent angle in air between the optic axes. The angle thus seen in air is conventionally known as 2E, and is often very large, and only in the widest-angle polariscopes and in cases of a small true angle are both axes visible at once in the field. When the crystal is immersed in oil, monobromonaphthalene, or other highly refractive liquid, the apparent angle is reduced, and both axes are more frequently capable of being brought to be visible in the field at once.

It has been shown in Chapter XLI. that of the two rays into which a beam of light is converted—as the effect of double refraction, on traversing a doubly refractive biaxial crystal along a direction lying in that principal section of the optical ellipsoid which has for its axes the directions corresponding to the minimum and maximum indices of refraction α and γ, and which also contains the two optic axes—one of them, vibrating perpendicularly to this plane, resembles an ordinary ray as it has the constant intermediate refractive index β in all directions; the other, vibrating in the optic axial plane, is an extraordinary ray, its refractive index varying from α to γ, and along the directions of the two optic axes it has the value β, the same as the perpendicularly vibrating ordinary ray. Hence, if we know the value of this intermediate index β of the crystal we can convert the apparent angle 2E of the optic axes into the real angle $2V_a$ by calculation with the aid of the formula:

$$(a) \qquad \sin V_a = \frac{\sin E}{\beta}.$$

Moreover, when the apparent angle in air is too large for the emergence of the optic axes, but the latter are visible when the section-plate is immersed in oil or monobromonaphthalene, if we also know the refractive index μ of this immersion liquid, we can calculate the true angle $2V_a$ from the apparent angle $2H_a$ in the liquid by means of the formula:

$$(b) \qquad \sin V_a = \frac{\mu}{\beta} \sin H_a.$$

If we prepare another section-plate perpendicular to the obtuse bisectrix of the optic axial angle, the axes will probably be invisible in air, but in the highly refractive liquid the angle will usually be sufficiently reduced to enable the axes to be seen, and the angle itself,

$2H_o$, to be measured. If μ and β be known we can find $2V_a$ at once from this observation alone, from the formula :

$$(c) \qquad \cos V_a = \frac{\mu}{\beta} \sin H_o.$$

Now, the knowledge of both the apparent acute and apparent obtuse optic axial angles, $2H_a$ and $2H_o$, thus obtained for liquid immersion enables us at once to calculate the true angle between the optic axes within the crystal, without requiring to know either the refractive index of the liquid or the β index of the crystal. For if, as before, $2V_a$ represent this true acute angle, $2H_a$ the apparent acute angle as measured while the plate perpendicular to the first median line is immersed in the liquid, and $2H_o$ the apparent obtuse angle similarly measured while the plate perpendicular to the second median line is immersed in the same liquid, in immediate succession before the temperature has had time to change, then :

$$(d) \qquad \tan V_a = \frac{\sin H_a}{\sin H_o}.$$

That is, the quotient of the sines of the halves of the two measured angles gives the tangent of half the true angle, the whole true angle being thus obtained by doubling the angular result of the calculation. The proof of this is at once afforded by dividing the equation (*b*) by the equation (*c*), the left part of the former by the left part of the latter, and similarly the right by the right. The terms $\frac{\mu}{\beta}$ cancel, leaving equation (*d*).

This method is of fairly general application, but it fails when the true angle is so small that the apparent obtuse angle, even in monobromonaphthalene or methylene iodide, is too large to be measurable, owing to the axial brushes not emerging or not being able to be brought into the centre of the field, the necessary rotation of the section-plate approaching very close to 90° on each side. In this case, however, if a liquid can be found of the same refractive index for sodium light as the mean index of the crystal, that is, the mean of all three indices α, β, and γ, for sodium light, the acute angle for this same light, as measured in this liquid with the plate perpendicular to the first median line, will be the true angle, and for other wave-lengths will be approximately the true acute angle ; and if the dispersions of the crystal and liquid are similar, the true angle will be afforded for all wave-lengths.

If a liquid of exactly the same refractive index as the mean crystal index be not available, observations may be made in the two liquids available of nearest indices, one slightly higher and one slightly lower, and the mean of the results taken, or a proper proportionate intermediate value.

Indeed, it is not always necessary to cut a section-plate at all, if such a perfectly matched liquid (or pair of liquids) be available, although it is usually much preferable to do so if possible. For the interference figure is seen almost as well through the whole crystal itself, when immersed in a parallel-sided cell of liquid of the same refractive index ; the edges and faces of the crystal almost perfectly disappear if the crystal

be colourless. This fact is of great use in the investigation of microscopic crystals, as we shall see later in Chapter LIII.

It is frequently possible to produce a liquid of exactly the same refractive index as the mean index of the crystal, for the middle of the spectrum (conveniently for sodium light), by mixing two liquids of higher and lower refraction, assuming of course that the two liquids are readily miscible and that they are without any mutual interaction. It is very convenient to have a ready means of determining approximately the refractive index of a liquid, especially the product of such a mixture, and a simple apparatus for the purpose was described and exhibited by Dr. Thomas and Mr. A. F. Hallimond at the meeting of the Mineralogical Society on November 9, 1920. The essentials are a telescope and collimator, such as those of any goniometer, arranged in the same straight horizontal line, as when taking a direct reading of the slit; a Websky slit is employed as usual, and a linear horizontal scale is added at the focus of the eyepiece. On a little adjustable stand between the optical tubes a parallel-sided and fairly narrow rectangular glass cell is supported, for the reception of the liquid, and in it is placed upright (on its base) at the middle of the cell a little isosceles triangular right-angled prism of glass of known refractive index; it fits the cell closely, the hypotenuse face resting against the side of the cell nearer the objective of the telescope, and the 90°-edge formed by the two equal faces (each at 45° to the hypotenuse face) just touching the farther side of the cell. Several such prisms, of suitably different refraction to form a series of reference indices, are provided. When the prism chosen is in position in the cell, and the liquid is added, if the latter be of the same refractive index a single image of the Websky slit is seen through the telescope, at the scale zero in the centre of the field, just as when cell, prism, and liquid are absent. But if the refractive indices of liquid and prism be different two images are seen, one on each side of the centre, and the scale, previously calibrated with liquids of known refractive index, affords by its readings for the two images, and a reference to the calibration curve, the actual refractive index of the liquid.

It is possible to calculate the optic axial angle from the three refractive indices α, β, γ, when the latter are known, by means of either of the formulæ:

$$\tan V_a = \frac{\gamma}{\alpha}\sqrt{\frac{\alpha^2-\beta^2}{\beta^2-\gamma^2}} \quad \text{or} \quad \cos V_a = \sqrt{\frac{\frac{1}{\beta^2}-\frac{1}{\gamma^2}}{\frac{1}{\alpha^2}-\frac{1}{\gamma^2}}}.$$

Only an approximate result is afforded, however; for a slight error of a unit or two in the fourth place of decimals of the refractive index causes a relatively very large difference in the optic axial angle. Hence, this method of arriving at the optic axial angle is only for use in the last resort, when no direct measurement is possible. An experimental determination is usually possible, however, and is infinitely more valuable and to be preferred.

The best form of polariscope for the measurement of 2E, $2H_a$, and $2H_o$ is the larger optic-axial-angle goniometer constructed by Fuess. This excellent instrument is shown in Fig. 759, and also in Fig. 760 as employed with the spectroscopic monochromatic illuminator and lime-light lantern. It is also shown in Fig. 761 with the electric lantern, the arrangement of the whole apparatus being that now always adopted by the author; this illustration also shows the apparatus for heating the crystal when it is desired to repeat the measurements at higher temperatures.

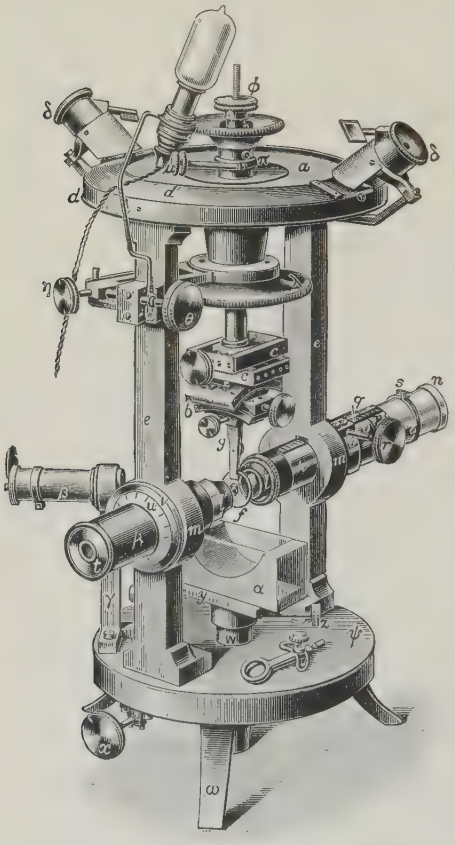


FIG. 759.—Larger Optic-axial-angle Goniometer.

The instrument is essentially a combination of the horizontal-circle goniometer and a polariscope. The circle *a* is the same as that of the No. 2*a* Fuess goniometer, and the crystal-adjusting [1] apparatus *b* and centring apparatus *c* is also similar, but is suspended below the circle instead of rising above it, the vernier table *d* and covering bevel-case *d'* for the circle being supported by two rigid wide columns *e*. The crystal, mounted on its little circular glass plate *f*, is suspended from the crystal-holder *g* below the adjusting and centring movements, and the polariscope *hk* is arranged at the same height with its horizontal axis parallel to a diameter of the circle. It consists of a polarising tube *h* with convergent lens system *l*, in this instrument a single hemispherical lens, and in the same axial line an analysing tube *k* with a similar lens system *l'* (also a simple hemisphere of glass in this polariscope), to collect the light rays again after their passage through the crystal suspended between the two tubes and their lens systems. Each tube is held in a collar *m* forming part of one of the columns *e*, which is widened at this height and pierced for the passage of the optical tube.

The polarising tube *h* carries an objective lens *n* at its outer end, where the light

[1] It is a great advantage to have the two circular adjusting movements graduated, as in the case of the author's cutting and grinding goniometer (Figs. 702 and 705, pages 933 and 942). The measurement of horizontal dispersion of the median lines is thereby rendered very simple, for instance. The upper fixed cylindrical segment of each should carry a divided silver arc, and the lower movable part of each an indicating mark (normally opposite the zero central position) also engraved on silver.

enters from the white-light goniometer lamp or the monochromatic illuminator; then comes the polarising Nicol prism in the middle of the optical tube, and subsequently,

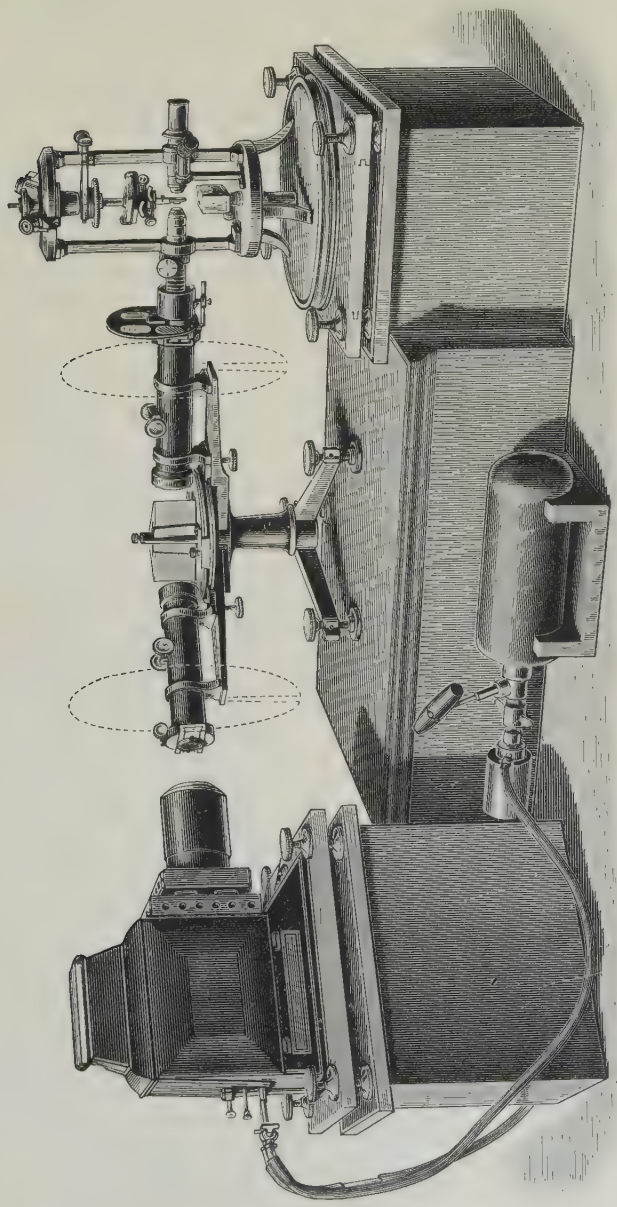


FIG. 760.—Determination of Optic Axial Angles with the Aid of the Monochromatic Illuminator and Lime-light Lantern.

about an inch from the inner end of the tube nearest the crystal a second lens similar to the first. Within this inner end there fits finally a short tube bearing at its extremity

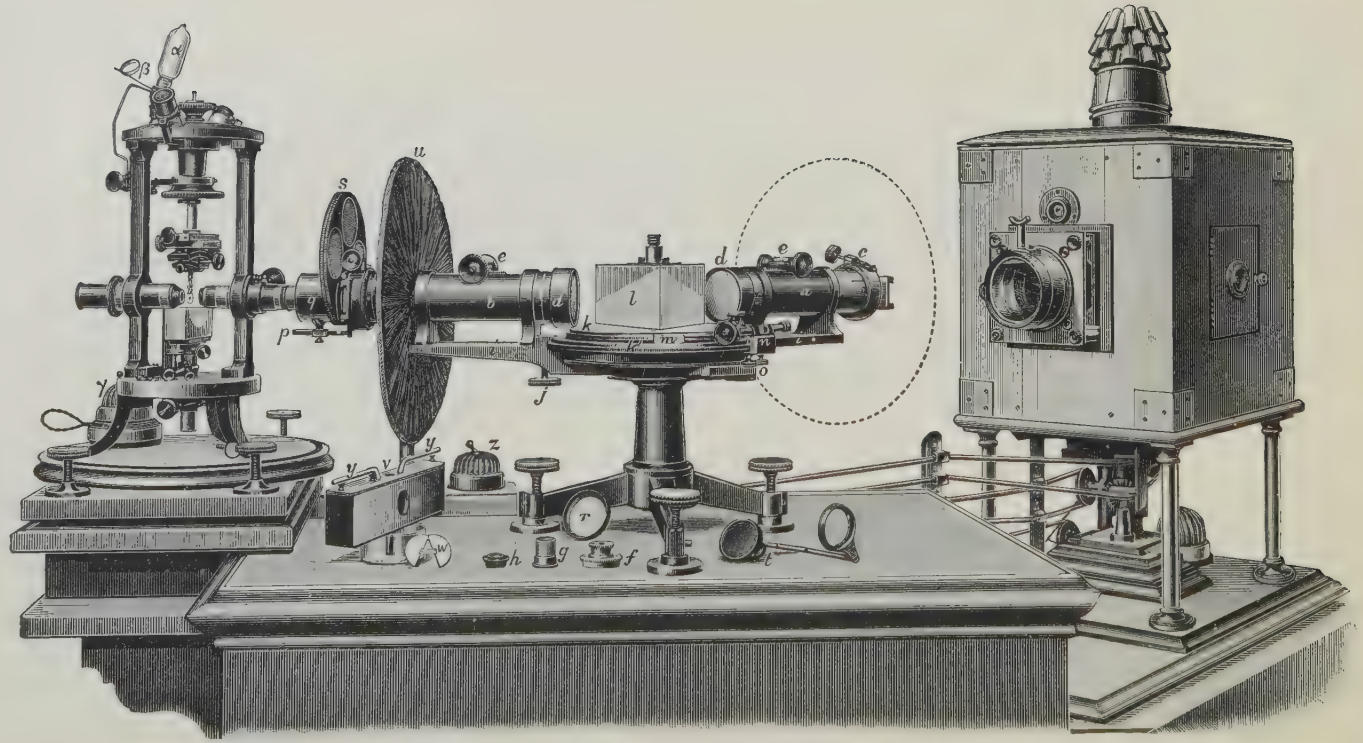


FIG. 761.—Apparatus for Measurement of Optic Axial Angles at the Ordinary and Higher Temperatures, employing the Electric Arc as Source of Light.

nearest the crystal the hemispherical lens l, with its plane side next to the crystal. The collar m supports this polarising tube in an outer tube o rigidly attached to m; and a second short inner tube p slides within o by rack q and pinion r, by which the polarising tube h itself, fitting tightly in the rack-tube p, can be racked closer to or further away from the crystal as may be required for the production of the best-lighted field of interference rings and brushes. The rack-tube has two notches in it, at 45° apart, and the polarising tube carries a tightening collar s bearing a corresponding projection, so that the tube may be automatically arranged with the plane of polarisation of the Nicol horizontal (or vertical) or at 45° thereto.

The analysing tube k comprises the inverted duplicate hemispherical lens l' (plane side towards the crystal) as convergent system, an adjustable glass plate bearing the engraved cross-lines—one horizontal and two vertical lines, the latter an apparent couple of millimetres apart—the eyepiece t and the analysing Nicol, the latter rotatable and provided with a bevelled silver circle u moving over a flanged collar v bearing also on silver the indicator mark. The collar is grooved and the outer tube of the analysing Nicol correspondingly keyed, to prevent rotation when the Nicol is rotated.

In the centre of the basal table is a bored cylindrical column w, adjustable for height by means of a rack and pinion x, and in the bore of which may be inserted the peg of a small rectangular table y, clamped by the screw z, to support the parallel-sided cell α for the highly refractive liquid to be employed as immersion liquid during some of the determinations. A little collimator tube β is also mounted on a separate column γ, about 35° to the left of the analysing tube, bearing a cross-line signal on glass instead of a slit, for occasional use in obtaining a reflection from a crystal-plate which it is desired to arrange normally to the axis of the polariscope tubes.

The circle is read by the two microscopes δ, and is fixed by the clamping screw η, and finely adjusted by the screw θ. The rotation of the circle is accomplished by the large milled wheel λ; it may also be clamped to the crystal axis by the tightening screw μ of the locking collar π. The crystal axis may be raised or lowered by means of the milled head ϕ at the summit of the instrument, and fixed at the desired height by a tightening screw and collar not shown (below λ). The whole is mounted on a stout base ψ with three feet ω.

This instrument has been found most satisfactory, in the form here described, for the measurement of optic axial angles. Some later innovations in the construction of the polariscope introduced by Fuess have not, in the author's opinion, been improvements. The small illuminating spectroscopic attachment provided with it is of little use, especially in cases of optic axial angles of wide or crossed-axial-plane dispersion. But the parts just described form the best and most delicately accurate goniometrical polariscope with which the author has ever experimented, and when used with the spectroscopic monochromatic illuminator described in Chapter XLIV. and shown in position in Figs. 760 and 761 the apparatus works to perfection.

When it is desired to conduct the determinations for higher temperatures than the ordinary, the little table supporting the cell of liquid is replaced by a metallic air-bath fitting, shown at v in Fig. 761 on the plinth of the monochromatic illuminator. It is an elongated rectangular box, the top of which is divided in the middle so as to be capable of being drawn off in two halves, a half from each side, leaving the centre open for the lowering of the crystal-plate into the middle of the bath, after which the two cover-slides can be slid in their grooves (cut in the upper edges of the sides) back again so as to close up the bath. A semicircle is cut out of each half of the cover at its inner end in order that the two parts may close together without quite touching the

crystal-holder, which thus passes readily through the circular hole formed by the approximation of the two halves. To ensure still better closing of the hot-air chamber a split disc, *w* in Fig. 761, hinged at one extremity of the diameter along which it has been cut, and with a square hole in the centre the exact shape of the section of the crystal-holder, may be fitted round the latter so as to rest loosely on the top of the bath over the circular aperture. A window *x* filled with truly plane-parallel glass is arranged at the centre of each side of the bath, opposite the optical tube in each case, the plane surface of the hemispherical lens of which is brought up to within a couple of millimetres of it during a determination. Each of these windows is fitted in a circular cap, screwed into the box side, and with just sufficient play to permit of the different expansion of the metal and glass during the heating. Two thermometers *y*, bent at an angle near the bulbs, may be introduced through two other holes near the central aperture, the stems being supported horizontally on two little stirrup-rests standing up from the lid in each case, while the bulb is within the bath quite close to the crystal. The author employs two miniature Bunsen burners to heat the apparatus, one near each end, the gas supply, regulated by a Stott governor and a graduated tap with lever-indicator, being delivered equally to them from a T-piece, on each side of which is a screw pinch-cock to effect any desirable separate control of the minute flames in order to ensure equal temperatures in the bath on each side of the crystal, as indicated by the two thermometers.

The conduction of heat by the crystal-holder is a serious matter when the crystal-plate or its glass mount is held directly by the clip-holder, but is considerably reduced by the use of a platinum holder, constructed out of thick foil and held firmly by the ordinary clip-holder, or better still in one of hard non-conducting boxwood replacing the ordinary holder. The correction for conduction under these conditions was determined in the case of the author's instrument by suspending the bulb of a miniature thermometer in the bath in the place of the crystal. The necessary correction was found, as the mean of several closely agreeing experiments, and even with all these precautions taken, to be as much as 7° in the neighbourhood of 100° C.

Another apparatus for determining the optic axial angle at temperatures higher than the ordinary, by hot liquid immersion, is described on page 1069 and illustrated in Fig. 778, which enables the exact temperature of the crystal to be determined directly, thus entirely avoiding this large correction inseparable from the use of an air-bath.

The angle taken in by the above described optic-axial-angle goniometer for accurate work is necessarily small, in order to ensure adequate refinement of measurement, and the much wider angle afforded by the polariscopical goniometer of the von Groth universal apparatus renders that instrument preferable for demonstration work. It is shown in Fig. 762 partly in section and with the optical tubes separately exhibited in section below, and in Fig. 763 in position in front of the monochromatic illuminator. It includes a much wider field, embracing both optic axes at once with their complete system of lemniscates, unless the apparent angle 2E between the optic axes be uncommonly large, corresponding to a true angle $2V_a$ of nearly 90°. This instrument may also be used for measuring the optic axial angle, but one must then be content with a lower degree of accuracy.

The optical tubes of this apparatus designed by von Groth and constructed by Fuess have already been partially described in connection with the stauroscope discussed in Chapter XLV. and shown in Fig. 723 (page 975). The polarising tube *i* bears the two lenses *j* and *k* with the large Nicol prism *l* between them just as in the stauroscope. But immediately after the lens *k* the condensing system of four lenses *a*, *b*, *c*, *d* follows closely, each mounted separately in its own screw cap so that it can be readily detached or added, according to the amount of convergence required to produce the most suitable rings and brushes with any particular section-plate, the number and closeness of the rings depending largely on two factors, the thickness of the plate and the

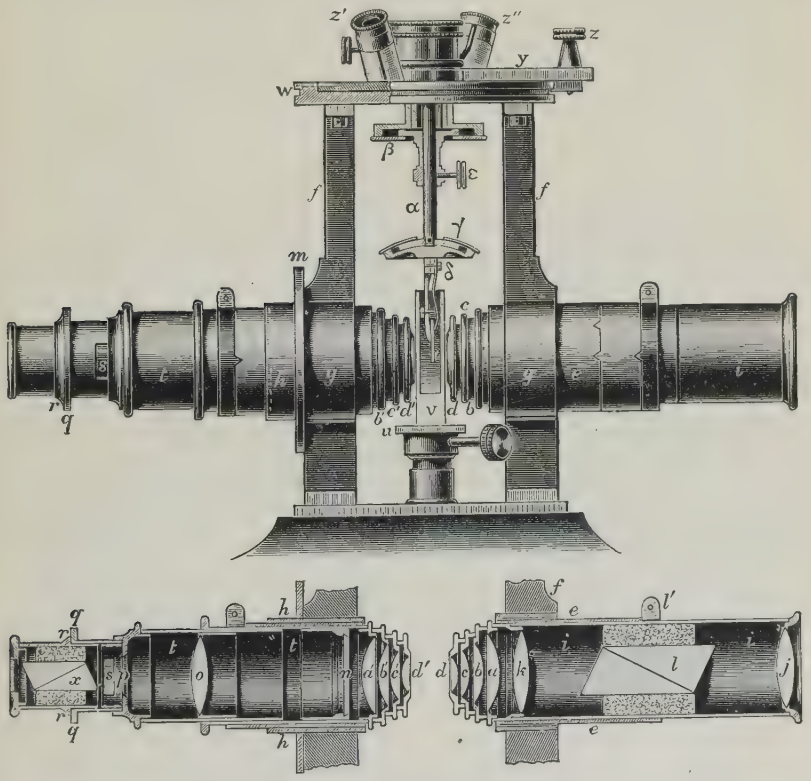


FIG. 762.—Optic-axial-angle Goniometer of the von Groth Universal Apparatus.

amount of the double refraction, the former varying inversely as the latter. This polarising tube slides freely in a short outer tube *e* carried rigidly by one of the two columns *f* of the instrument, each of which is cast with a ring expansion *g* just below the centre, in which ring the outer tube is screwed. This outer tube bears two notches at 45° apart, to fit a V-projection on a tightening collar clamped round the polarising tube, so that when the plane of polarisation of the Nicol has once been determined, the tube can be inserted with this plane either vertical or obliquely at 45°.

The analysing tube *t* is supported in a similar manner in an outer tube *h* carried by the ring expansion *g* of the other column, and a couple of notches are cut in the outer tube at 45° apart to gear with a corresponding V-projection on a collar carried by the analysing tube. Moreover, there is a vertical vernier-plate *m* for a circle,

carried round the outer tube and close up to and in front of the ring of the column, in order that a cap provided with a large bevelled silver divided circle may fit over it; this special cap bears a short tube, in which the analysing Nicol prism x to be presently referred to, together with its carrying tube, may be inserted, when the instrument is to be used for another purpose to be described in Chapter L., that of determining the angle of rotation of the plane of polarisation of light by a plate of an optically active crystal (see Fig. 794, page 1087).

The analysing tube carries at the end nearest the polarising tube and the crystal a series of four short focus lenses a', b', c', d', similar in every respect, including focal length and curvature, to those of the polarising tube. Just beyond the fourth provision is made for the adjustable insertion of a glass plate n bearing an engraved scale, which can be calibrated, by comparison with the interference figures of crystals of known optic axial angle, so that the value of the divisions in optic-axial-angle magnitudes

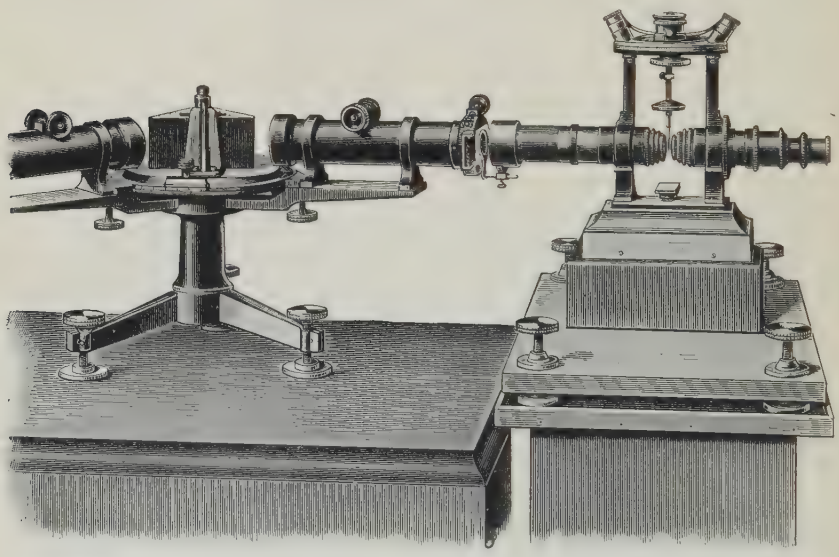


FIG. 763.—The Wide-angle von Groth Apparatus arranged with Monochromatic Illuminator for the Measurement of Optic Axial Angles or Observation of the Interference Figures.

shall be known. This is best removed if the instrument has to be used either for real measuring of the optic axial angle by the attached goniometer, or for the study or photography of the interference figures, as it disturbs the beauty of the interference figures. Further along the tube is the viewing lens o, carried in an adjustable inner tube, slotted to gear with a pin in the main tube in order that no rotation shall be possible. The scale n is situated at its focus. A diaphragm p follows a little distance further, where the inner tube narrows and eventually terminates in a flange q which gives it a broad flat end, which is silvered and engraved with an indicator mark for the circle of the analysing Nicol x. This latter is carried in a short tube provided with a flange bearing the bevelled silver divided circle r. The narrow part of the inner tube close to the thicker part has a pair of slots s cut in it at positions diametrically opposite to each other and which, when desired, can be inclined 45° to the vertical and horizontal directions, for the reception of a mica quarter-undulation plate or a quartz wedge. The slots can be closed by a rotating inner cylindrical

shutter, manipulated by a pin projecting through one of the slots, when the mica or quartz is not required.

The base of the instrument carries in the centre under the crystal a little table u, adjustable for height by means of a rising and falling column, in order that the crystal may be immersed in a cell v containing a highly refractive liquid, such as monobromonaphthalene, for the measurement of $2H_a$ and $2H_o$.

The two columns carry at their upper terminations the goniometer circle w, divided on its wide silver limb directly to 20′, and reading to single minutes with the aid of a vernier carried on a similar flat and broad silver limb moving concentrically within the circle plate and flush with it. Rotation of this vernier disc is effected by means of a lever arm y carrying a large milled head z, which is the head of a clamping screw by which the vernier and circle-plates may be clamped together with the aid of a small bracket-piece fitting a groove in the periphery of the circle-plate. Around the central boss of the vernier plate, from which the arm radiates, a ring is loosely fitted, having two light arms branching off opposite to one another and terminating in holders for a couple of small microscopes z' and z'', with which to read the circle at diametrically opposite positions.

Within the central boss there is capable of either independent or clamped rotation the axis a, terminating in the crystal-holder and carrying the means of adjustment of the crystal. The nature of the centring and adjusting movements will be clear from Fig. 762. They are both simple movements of a sliding character, the centring movement β being that of a flat circular disc within a flat circular box of large diameter, and the adjusting movement γ that of a shallow cup-shaped disc of spherical curvature within a similarly shaped box, the disc being fixed to the axis and the box being movable about it in this case; both boxes have on one side (the lower and the upper in the two respective cases) six radial saw-cuts in three pairs close together so as to grip the discs by three strips which can be slightly bent in. The adjusting movement is carried just above the crystal-holder δ, one of the usual spring gripping type, and from its disc rises the inner axial rod α, which slides within a short wider tube carried below by the centring disc β, which is pierced in order that a long length of inner axis α may be available. A fixing screw ϵ enables the axis to be clamped at the right height for the most perfect passage of the rays from the polariser through the crystal.

A heating apparatus consisting of a rectangular bronze air-bath, similar to that of the larger optic-axial-angle goniometer, is provided for use with the instrument. As the convergent system, when all the lenses are employed, is a much more powerful one, however, than that of the polariscopical goniometer just referred to, the two optical tubes require to be brought with their convergent systems closer together, nearer to the crystal. Hence, the two circular parallel-plate glass windows are fitted in circular frames tapped with a screw thread on their periphery, to fit similar threads in the two circular apertures facing each other in the box sides, so that by means of a key provided they may be screwed more or less deeply into the box, and thus enable the two convergent systems to penetrate adequately within the box without quite touching the window.

As an example of an actual determination the measurements and results of the calculations may be quoted for the optic axial angle of monoclinic ammonium magnesium sulphate. The plane of the optic axes of the crystals of this salt is the symmetry plane, and the first median line (acute bisectrix of optic axial angle) is inclined 12° 8′ to the axis a, and the second median line (obtuse bisectrix) is inclined 4° 58′ to the vertical axis c, in front of the latter.

Determination of Optic Axial Angle of $(NH_4)_2Mg(SO_4)_2 . 6H_2O$.

With Section-plate Perpendicular to Acute Bisectrix.		With Section-plate Perpendicular to Obtuse Bisectrix.
Apparent Angle in Air 2E.	Apparent Angle in Monobromonaphthalene $2H_a$.	Apparent Angle in Monobromonaphthalene $2H_o$.
Li-light 79° 15′	45° 21′	106° 35′
C „ 79 14	45 18	106 30
Na „ 79 10	44 56	106 0
Tl „ 78 59	44 38	105 28
F „ 78 44	43 57	104 35

Calculations.

	Calculated Value of V_a.	Calculated Value of $2V_a$.
Expression for $\tan V_a = \frac{\sin H_a}{\sin H_o}$.		
For Li-light, $\tan V_a = \frac{\sin 22° 40\frac{1}{2}'}{\sin 53\ 17\frac{1}{2}}$	25° 41′	51° 22′
C „ $= \frac{\sin 22\ 39}{\sin 53\ 15}$	25 40	51 20
Na „ $= \frac{\sin 22\ 28}{\sin 53\ 0}$	25 34	51 8
Tl „ $= \frac{\sin 22\ 19}{\sin 52\ 44}$	25 30	51 0
F „ $= \frac{\sin 21\ 58\frac{1}{2}}{\sin 52\ 17\frac{1}{2}}$	25 19	50 38

The values of $2V_a$ derived from the measurements of two other pairs of section-plates were within a few minutes of the values just given in the last column, and the final mean values for $2V_a$ derived from all three sets of determinations are set forth below :

Li-light . . .	51° 20′
C „ . . .	51 18
Na „ . . .	51 11
Tl „ . . .	51 2
F „ . . .	50 36

The values for G-light are not as a rule adequately accurately determinable in monobromonaphthalene, owing to the absorptive power of the liquid for violet light.

Determination of the Dispersion of the Median Lines. Case 1. Inclined Dispersion of both Median Lines (both lying in the symmetry plane).—The theoretical discussion of this subject, which concerns only monoclinic and triclinic crystals, has already been given in Chapter XLII., p. 927, and the three cases possible to monoclinic crystals explained ; hence it only remains here to describe the practical operations involved in the determination.

It will be obvious that the first median line can only be truly perpendicular to the section-plate for one colour, and the plate is generally cut truly for sodium light, a convenient radiation not very far from the middle of the spectrum, and one for which under any circumstances the stauroscopic observations will have been made. The amount of the dispersion is usually very small, rarely exceeding a degree and generally only a few minutes, and consequently too small to introduce any appreciable error in the measurement of the optic axial angle for wave-lengths other than that of sodium light. It is so small, indeed, as a rule, as to be almost undetectable in the determination of the extinction directions in the symmetry plane by the stauroscope for red light and for blue light, and this is, therefore, by no means a method of precision for determining such a small amount of dispersion of the median lines.

In order to determine it accurately, after measuring the optic axial angle in the ordinary manner just described for the usual wave-lengths, including the limiting wave-lengths between which we wish to find the dispersion, we also measure the separate movement of each optic axis while the crystal is immersed in a liquid of the same refractive index for sodium light as the mean index of the crystal. The series of measurements in monobromonaphthalene do not serve for both purposes, because the dispersion of the axes varies with the liquid, and the true angle within the crystal is only afforded when the refractive index of the liquid is the same as that of the crystal.

The crystal axis of the optic-axial-angle goniometer is rigidly locked to the circle during the measurements, and the orientation of the section-plate is also carefully noted as regards the crystal faces, so as to ascertain in which direction the dispersion of the median line occurs. For this reason it is always advisable to leave as many faces uninjured on the edges of the section-plate as possible, to be used as reference faces during these measurements, that is, to inform us on which side, right or left, of the adjusted section-plate the crystallographic axes *a* and *c* are situated. From the actual circle readings for the positions of the two optic axes for red Li-light or C-light and for greenish-blue F-light (the angle for G-light being rarely obtainable with adequate accuracy on account of the feebleness of the light escaping absorption) the movement of each axis can be readily found, and the mean of the two determinations (or the half of their difference) for the two axes is taken as the amount of the dispersion of the first median line.

The measurement of the optic axial angle in a liquid of the same refractive index is also of use as indicating, at any rate approximately, the magnitude of the true angle $2V_a$, and of confirming the order of dispersion of the axes, as shown by the calculated results of $2V_a$ from $2H_a$ and $2H_o$, even in the cases of rhombic crystals, whenever the variation of the optic axial angle for different wave-lengths is very small, a few minutes only for instance.

The example of monoclinic ammonium magnesium sulphate may again be taken as an illustration as regards the determination of

inclined dispersion; for the optic axes of the crystals of this salt lie in the symmetry plane. The mean refractive index (mean of all three indices α, β, γ for sodium light) is 1·4744. From the list of refractive indices given on page 810 in Chapter XXXVII. it will be observed that oil of turpentine has a refractive index of 1·4725 at 20°, and at the temperature of the experiment, about 15°, the index of this liquid is 1·474. It is thus particularly suitable for the purpose. Observations in this liquid with the same section-plate as was used in the measurements in monobromonaphthalene quoted on page 1048 showed that the first median line lay 17′ nearer to the a axis for red C-hydrogen light than for green F-hydrogen light.

Case 2. Horizontal Dispersion of the First Median Line.— The plane of the optic axes in this case is perpendicular to the symmetry plane and the first median line lies in the symmetry plane and is dispersed in it, the second median line being the immovable symmetry axis b. When the crystal-adjusting segments of the polariscopical goniometer are graduated, as recommended on page 1040 (in the footnote), the measurement of horizontal dispersion is perfectly simple. For then that segment the vertical plane of movement of which is perpendicular to the section-plate only requires to be moved, and the movement read off on the silver arc, between the two positions when the optic axial interference figure is adjusted to the horizontal cross-wire, as if for the measurement of the optic axial angle, in light of the two extremes of the spectrum, say red C- and greenish-blue F-hydrogen light. The crystal should preferably be immersed in a liquid of the same refractive index during the measurement. The angle thus read off on the segment-arc is the dispersion of the first median line required, between C and F. As an example of the mode of conducting the measurement of the amount of horizontal dispersion when this simple method is not available, the adjusting segments not being provided with graduated arcs, the determination in the case of the monoclinic form of ammonium selenate $(NH_4)_2SeO_4$ may be quoted.

The section-plate was adjusted so that the line joining the two optic axes for sodium light was arranged vertically (on the vertical spider-line or its prolongation) instead of horizontally, and the Nicols were set at 90° and 0° instead of at 45° and 135°. Each of the optic axes in turn was brought to the centre of the cross-lines by rotation of the back-to-front cylindrical adjusting segment of the polarising goniometer, and measurements were then made of the lateral difference of position of the axis for the two limiting wave-lengths of light—in this instance red C- and greenish-blue F-light—by rotation of the circle (with the crystal) for the slight amount necessary to adjust the optic axis exactly to the centre of the spider-lines for the two colours in turn, while the plate was immersed in (1) oil of cassia ($\mu = 1·5862$) and (2) oil of anis ($\mu = 1·5540$), the refractive indices for sodium light of which two liquids are slightly higher and lower respectively than the mean index for sodium light of ammonium selenate crystals (1·5694). Both series of determinations (for the two separate optic axes) agreed in indicating that the two optic axes are dispersed 12′ between C-light and F-light, which, taking into

consideration the position of either optic axis between the fixed second median line (parallel to the immovable symmetry axis) and the movable first median line, as indicated by the optic axial angle (37° 19′ for C-light and 38° 44′ for F-light), corresponds to a dispersion of the first median line of 13′, as will next be shown.

The problem is to find the angle θ in the spherical triangle in Fig. 764, in which B_{aC} and B_{aF} are the two positions of the movable acute bisectrix for C- and F-light respectively, B_o is the immovable obtuse bisectrix, C the position of one of the optic axes (that lying in this quadrant) for C-light and F the same for F-light. The actual 12′ angle measured was the line CF at right angles to the base B_oCB_{aC}, that is, the displacement of the optic axis parallel to the horizontal cross-wire, which is parallel to B_{aC} B_{aF}, the angle required between the positions of the first median line for the two wave-lengths. Now this latter required angle is the angle θ, and from the data now acquired it can be calculated at once. For FCB_0 is a spherical triangle with a right angle at C, the side CB_o is the complement of V_a for C-light which is 18° 40′, and the short side CF is the measured 12′. Hence, constructing a Napierian diagram (Fig. 765), we obtain from it the relation :

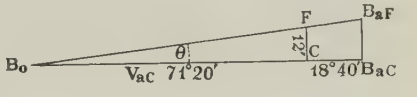


FIG. 764.

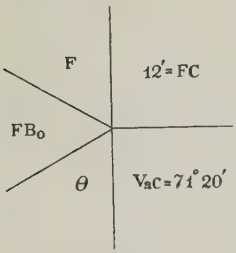


FIG. 765.

$$\sin 71° 20′ = \tan 12′ . \cot \theta \; ; \text{ and } \cot \theta = \sin 71° 20′ \cot 12′$$

Log. sin 71° 20′ = $\bar{1}$·97653
Log. cot 12′ = 2·45709

Log. cot θ = 2·43362 $\theta = 13′$.

Thus, in cases like this, where the horizontal dispersion is very small, this calculation is not absolutely necessary, for the difference of one minute between 12′ and 13′ is less than the possible error in determining the amount of horizontal displacement of the optic axis experimentally. Hence, when the angle is small the displacement of the first median line may be taken as being sensibly afforded by the displacement of either of the optic axes. After some experience with optic axial angles and dispersions of different magnitudes it is, however, quite possible to draw up a scale of these minute corrections. Until this information has been accumulated, however, it is safest to make the simple calculation in every case. The largest amount of horizontal dispersion met with by the author in his investigations is 3° 50′, in the case of cæsium magnesium chromate, $Cs_2Mg(CrO_4)_2 . 6H_2O$, and the following account of its measurement is taken from the memoir[1] on the subject :

[1] *Mineralogical Magazine*, 1912, *16*, 169.

"The section-plate—the orientation of which was clearly known from the crystal-faces left on the edges—was arranged so that the plane of the optic axes was vertical, and the planes of the Nicols were made vertical and horizontal. The section was then tilted by one of the adjusting segments until one of the optic axes, as seen first in monobromonaphthalene and subsequently in acetylene tetrabromide, was adjusted to the horizontal cross-wire. It was then brought exactly to the vertical wire for red lithium-light, and next for green cadmium-light, by rotation of the goniometer circle, and the readings of the latter for each position taken. The difference of the readings was the apparent dispersion of that optic axis in the liquid employed. Monobromonaphthalene has a somewhat higher refractive index (1·6657 for sodium-light), and acetylene tetrabromide a somewhat lower one (1·6380), than the mean crystal index (1·6447), and the mean of the indications may be taken as the true value. It proved to be 3° 14′ in the latter liquid and 3° 10′ in the former one, so that the mean 3° 12′ may be safely taken as the true dispersion of that axis. Similar operations carried out with the other optic axis gave an identical result. The direction is such that the median line will be nearer to the vertical axis c for green cadmium-light than for red lithium-light. The semi-optic-axial-angle for sodium-light being 33° 32′, the dispersion θ of the median line is given by the formula: $\cot \theta = \sin (90° - 33° 32') \cot 3° 12'$, from which θ is found to be 3° 50′. Hence, the first median line is dispersed in the symmetry-plane so that it is nearer to the vertical axis c by 3° 50′ for green cadmium-light than it is for red lithium-light. An identical result was obtained by determining also the position of the axes for sodium-light, and then calculating the difference of position for lithium-light on one side and for cadmium-light on the other. The sum of the two was 3° 50′."

Case 3. Crossed Dispersion of the Second Median Line.—The plane of the optic axes is again perpendicular to the symmetry plane, but the movable bisectrix lying in the symmetry plane is now the second median line instead of the first. The measurement of the displacement is carried out just as for case 2, except that it is the plate perpendicular to the second median line which is employed, instead of the one perpendicular to the first median line.

Use of the Quarter-wave Mica Plate and Quartz Wedge for the Determination of the Sign of the Double Refraction.—When the quarter-wave mica plate referred to in Chapter XLII., in the form of the 6 by 1 centimetre strip described on page 912, is inserted diagonally at 45° to the planes of the crossed polariser and analyser, during the examination of the section-plate of a uniaxial crystal perpendicular to the axis in convergent polarised light, the mica being inserted between the crystal-plate and the analyser, the figure is altered in opposite ways in alternate quadrants. The $\frac{1}{4}\lambda$ effect of the mica is added to that of the crystal in one pair of quadrants, and subtracted from it in the alternative opposite pair. It has to be remembered that the quarter-wave mica plate transmits two rays, one vibrating more slowly parallel to the axis γ of the indicatrix (parallel to the length of the 6 cm. by 1 cm. plate), and

the other vibrating more rapidly at right angles to the first, parallel to the axis β of the indicatrix (parallel to the ends of the plate), the total difference of phase being exactly $\lambda/4$. Supposing the elongated mica plate, indicated by the crossed arrow, to be arranged as shown in Fig. 766, passing across parallel to the diameter bisecting quadrants 1 and 3, and that the crystal is of positive double refraction, the portions of the rings in these quadrants are contracted, and those in the other two quadrants to a similar extent expanded, the effect being to bring the dark (monochromatic light being used) arcs of any one quadrant opposite the illuminated arcs of the two adjacent quadrants, at the rectangular junctions; while if the crystal be negative the rings are expanded in the 1 and 3 quadrants and contracted in 2 and 4, as shown in Fig. 767. If white light be employed, the colours exhibited by the rings in adjacent quadrants are complementary. The dark cross, with arms parallel to the planes of the Nicols, vertical and

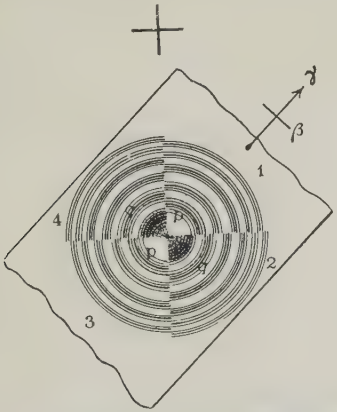


FIG. 766.—Effect of Quarter-wave Mica Plate on the Interference Figure of a Positive Uniaxial Crystal.

FIG. 767.—Effect of Quarter-wave Mica Plate on the Interference Figure of a Negative Uniaxial Crystal.

horizontal, also disappears, as a result of the circular polarisation which is introduced by the quarter-wave mica plate, and instead, whether monochromatic or white light be employed, the innermost portion of each quadrant in which the rings are expanded, that is, the apex of the quadrant adjacent to the centre, becomes a dark spot. A useful rule to remember is, that if the two spots lie on the diagonal line along which the mica strip is inserted, as in Fig. 767, the crystal is negative; whereas, when the two spots are on each side of that diagonal line, on a line at right angles to it (parallel to the short edges of the rectangular mica plate, and thus parallel to the β axis, and perpendicular to the γ axis of the indicatrix which joins the apparent positions of the two optic axes of the mica), as represented in Fig. 766, the crystal is positive. As an aid to the memory, it may be pointed out that the line joining the two spots makes with respect to the length of the mica plate the sign + in the case of positive crystals, and the sign − in the case of negative crystals. Another memory rule is, that the rings are enlarged and spots formed in those quadrants through

which the long direction line of the mica passes when the crystal is negative.

In explanation of these phenomena we may consider the case of a positive uniaxial crystal in convergent monochromatic polarised light. The original first dark ring, the position of which is indicated in Fig. 766 by a dotted circle, is produced owing to the retardation here of one of the two rays (into which the light from the polariser is resolved on entering the crystal) behind the other for a whole wave-length λ, an extra $\lambda/2$ difference being also added by the analyser, thus rendering the conditions those for darkness instead of light. Of the two rays the extraordinary is the slower one vibrating in the principal section, and the ordinary the faster one vibrating perpendicular to that section and to the optic axis. In quadrant 1 or 3 the effect of the introduction of the quarter-wave mica plate is to accentuate by $\lambda/4$ the difference of phase, so that a full wave-length of difference is already produced at a position p nearer the centre of the figure, so that with the aid of the analyser $(+\lambda/2)$ the conditions at p are those for a dark ring. Contrariwise, in quadrant 2 or 4, the difference of phase is diminished by $\lambda/4$ on introducing the mica plate, and the first ring will only be produced at q, further removed from the centre. The exact conditions will be clear from the scheme set out below.

Conditions on Introduction of $\lambda/4$ Mica Plate.

	For position p.		For position q.	
Mica	Long direction, of slower (slowest) ray γ.	Narrow direction, of faster (medium) ray β	Long direction, of slower γ.	Narrow direction, of faster β.
Crystal	Extraordinary, slower ray.	Ordinary, faster ray.	Ordinary, faster ray.	Extraordinary, slower ray.
Result of combination	Slower still.	Faster still.	Faster ray rendered not relatively so fast.	Slower ray hastened.
	Retardation of first ray behind second increased by $\lambda/4$.		Retardation of second ray behind first reduced by $\lambda/4$.	

Similarly, the radius of every further ring is diminished in the quadrants 1 and 3, and increased in quadrants 2 and 4.

In negative crystals the ordinary is the slower ray and the extraordinary the faster, so that the conditions are inverted, the radius of the rings in quadrants 1 and 3 being increased, and that of rings in quadrants 2 and 4 reduced.

An analogous effect is produced with a biaxial crystal-plate, as shown in Figs. 768 and 769. The crystal must be arranged with the line joining the pair of optic axes parallel to one of the planes of the crossed Nicols, and on inserting the mica plate diagonally as before, indicated by the dotted line MM, the following effects are observed. If the crystal be positive (the first median line being the γ axis of the indicatrix, and therefore the direction of least vibration velocity) two dark spots are produced adjacent to the horizontal diameter PP in the quadrants 2

and 4 in which the rings are expanded, that is, above the horizontal line on the left (fourth quadrant) and below (second quadrant) on the right; while if the crystal be negative (the first median line being α, the direction of maximum velocity), the spots will be conversely arranged, below on the left (third quadrant) and above on the right (first quadrant). A similar memory rule may be remembered as for uniaxial crystals, namely, that when the crystal is positive the rings are enlarged, and the spots appear, in those quadrants through which the direction line of the elongated mica plate does *not* pass; and that when the crystal is negative the ring expansion occurs, and the spots appear, in those quadrants which *are* traversed by the mica plate (that is, bisected by the diametral line representing the length of the mica plate).

It must be remembered as regards both the uniaxial and the biaxial

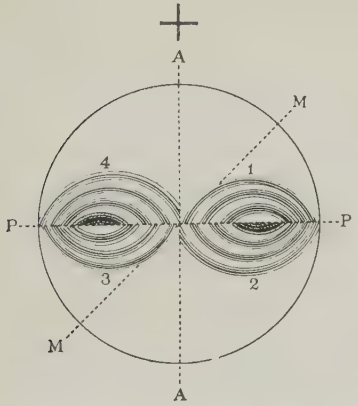


FIG. 768.—Effect of Quarter-wave Mica Plate on the Interference Figure of a Positive Biaxial Crystal.

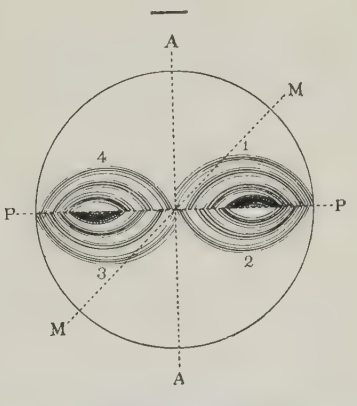


FIG. 769.—Effect of Quarter-wave Mica Plate on the Interference Figure of a Negative Biaxial Crystal.

figures, however, that the spots are not regarded as the beginnings of new rings, but as the remains of the black cross. They are black, indeed, in white light as well as in monochromatic light.

The interference figures afforded by a section-plate perpendicular to the second median line (in a highly refractive liquid) exhibit inverse phenomena as in Fig. 768 for a negative crystal, and as in Fig. 769 for a positive.

When two quarter-wave plates are employed, one before and one after the crystal-plate, both arranged with their γ-direction at 45° to the planes of vibration of the crossed Nicols, the dark cross of either a uniaxial or a biaxial figure will disappear altogether, and the rings appear alone and undisplaced, that is as continuous rings; in the case of a uniaxial crystal they are truly circular, exactly resembling Newton's rings or those afforded by a concave film of gypsum (selenite) or a concave plate of quartz. On rotation of the analyser the rings will expand or contract,

according to the direction in which the analyser is turned, very much like those of an optically active crystal such as quartz. These facts are true whether the light be monochromatic or ordinary white light, the only difference being that the rings are dark in the former case and spectrum coloured in the latter.

The sign of the double refraction of a biaxial crystal may also be determined by use of the quartz wedge also described in Chapter XLII. (page 914). Quartz being positive (uniaxial), it subtracts from the effect of a negative crystal, making it appear as if thinner, while it adds to the apparent thickness of a positive crystal. The crystal-plate is arranged at 45° to the crossed Nicols, and the quartz plate is inserted between the crystal-plate and the analyser, first along one and then along the other of the 45°-diagonals, that is, parallel to the direction of the line joining the optic axes and perpendicularly thereto. The latter case is shown for negative (biaxial) mica in Fig. 770. In this case the direction of the maximum γ axis of the optical indicatrix of the mica crystal coincides with that of the minor axis ω of the quartz, and thus the two effects are subtractive, so that the result is as if a thinner plate were being examined, and the rings will consequently expand. As the quartz wedge is pushed further and further in so as to increase the thickness of quartz in action, the rings will successively expand, and pass through the loop stage to the ellipse-like variety of lemniscate, one after the other.

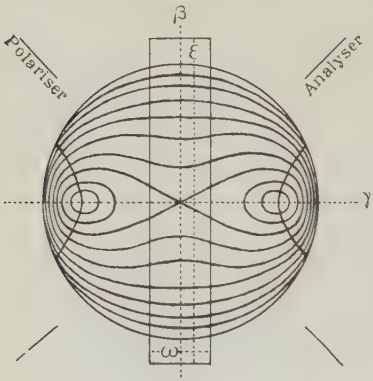


FIG. 770.

If the wedge be inserted parallel to the line joining the optic axes, the maximum axis γ of the crystal in the case of mica, this axis and the major axis ϵ of the wedge being in conjunction the effects are additive, and the appearance is that corresponding to a thickening of the section-plate, that is, a closing up of the rings.

The converse phenomena are observed when the crystal is a positive biaxial one, the rings expanding when the quartz wedge is inserted parallel to the line joining the optic axes, and contracting when the insertion occurs at right angles thereto.

The effect of the quartz wedge is most strikingly shown with section-plates too thick to show the optic axial rings. If the crystal be negative and not too extremely thick, the rings will make their appearance when the wedge is inserted perpendicularly to the line joining the optic axes, or if it be positive, when it is inserted parallel to the optic axial line.

In concluding this chapter it may prove convenient to give a short table of a few easily procurable substances exhibiting graduated values of the optic axial angle.

TABLE OF SOME USEFUL OPTIC AXIAL ANGLES FOR NA-LIGHT.

	2E.	$2V_a$.	Observer.
Nitre (potassium nitrate)	10° 51′	7° 12′	Schrauf
Cerussite (lead carbonate)	17 8	8 14	,,
Sanidine felspar	19 45	12 50	Des Cloizeaux
Aragonite (rhombic calcium carbonate)	30 52	18 11	Kirchhoff
Borax (sodium borate)	59 23	39 36	Tschermak
Potassium magnesium selenate (with $6H_2O$)	61 7	39 38	Tutton
Barytes (barium sulphate)	63 12	37 28	Heusser
Potassium copper sulphate ($6H_2O$)	72 7	46 32	Tutton
Potassium magnesium sulphate ($6H_2O$)	72 47	47 54	,,
Cæsium copper selenate ($6H_2O$)	77 33	48 26	,,
Ammonium magnesium sulphate ($6H_2O$)	79 11	51 11	,,
Ammonium sulphate	84 6	52 12	,,
Rubidium copper selenate ($6H_2O$)	85 49	53 11	,,
Ammonium magnesium selenate ($6H_2O$)	88 4	54 47	,,
Ammonium copper selenate ($6H_2O$)	90 50	55 7	,,
Topaz	100 40	56 39	von Kokscharow
Potassium cobalt selenate ($6H_2O$)	104 25	62 19	Tutton
Potassium sulphate	111 0	67 20	,,
Potassium zinc sulphate ($6H_2O$)	112 29	68 14	,,
Ammonium manganese sulphate ($6H_2O$)	116 23	69 49	,,
Potassium nickel selenate ($6H_2O$)	130 3	72 48	,,
Potassium nickel sulphate ($6H_2O$)	130 57	75 16	,,
Ammonium ferrous sulphate ($6H_2O$)	134 17	76 25	,,
Ammonium zinc sulphate ($6H_2O$)	144 41	79 0	,,
Ammonium ferrous selenate ($6H_2O$)	148 35	77 44	,,
Ammonium cobalt sulphate ($6H_2O$)	158 38	82 9	,,
Ammonium nickel sulphate ($6H_2O$)	Invisible	86 33	,,
Potassium copper selenate ($6H_2O$)	,,	88 27	,,

CHAPTER XLIX

CROSSED-AXIAL-PLANE DISPERSION OF THE OPTIC AXES

It has been made clear in the last chapter that the positions of the two optic axes of a biaxial crystal are in general different for different wave-lengths of light and at different temperatures, and mention was made of extreme cases in which the axes are separated at a considerable angle along one plane of the optical ellipsoid for red light or a particular temperature, and along another principal plane, necessarily at right angles to the first, of the ellipsoid for blue light or a second specific temperature. These instances are not so rare as they were formerly thought to be, and the author has met with and studied in detail no less than seven such cases in the course of his investigations, and from the experimental evidence has evolved the general law governing the phenomenon.[1] It was shown that the essential conditions for crossed-axial-plane dispersion are :

"(1) The simultaneous occurrence of extremely small double refraction (nearness of α and γ indices of refraction) and close approximation of the intermediate index β either to the α or to the γ index. The latter condition is necessary for the possibility of crossing, and the former for wide separation of the optic axes in the two planes for the two ends of the spectrum, or for two different temperatures. (2) Change of wave-length of the light employed at the ordinary temperature, or change of temperature while using light of the same wave-length, or both kinds of change simultaneously operating, must so act as to bring about equality, at a particular temperature for each wave-length, of two of the three refractive indices, namely, of the intermediate index β and of that one of the other two which is already nearest to equality with it."

It is the first condition which renders the crystal so sensitive to even minute physical change, such as is brought about as the result of the usual difference shown by the three indices in their spectral dispersion, and the slightly different effect of change of temperature along each of the axial directions of the optical ellipsoid, both of which causes are adequate to upset the balance. For when all three refractive indices are

[1] "Allgemeine Erklärung des Phänomens der Dispersion in gekreutzten Axenebenen," *Zeitschr. für Kryst.*, 1907, *42*, 554; "The Optical Constants of Gypsum at Different Temperatures," *Proc. Roy. Soc.*, A, 1908, *81*, 40.

so close together at the start, a change only affecting the fourth decimal place in the refractive index may suffice to reverse the relative positions of two of the indices, and thus for some intermediate wave-length or temperature to effect the temporary equality of those two indices, with production of uniaxial conditions, and display of the rectangular cross and circular rings by a section-plate perpendicular to what under ordinary conditions is the first median line, one of the three axes of the optical ellipsoid of general form, but which under the temporary conditions referred to becomes the axis of a rotation ellipsoid.

The crystals which exhibit crossed-axial-plane dispersion are more or less divisible into two main classes, which are respectively especially sensitive to change of temperature and to change of wave-length. Of the first class gypsum (selenite), the monoclinic hydrated sulphate of lime $CaSO_4 . 2H_2O$, is the most striking example; while clear cases of the second class are afforded by brookite, the rhombic form of dioxide of titanium, TiO_2, the so-called "triple" tartrate of potassium, sodium, and ammonium, the crystalline product obtained as an isomorphous mixture from mixed solutions of the rhombic double tartrates of potassium and sodium, and ammonium and sodium, known as the Seignette salts, $C_4H_4O_6KNa . 4H_2O$ and $C_4H_4O_6(NH_4)Na . 4H_2O$, and the rhombic picrates of iron and manganese, $[C_6H_2(NO_2)_3O]_2Fe . 5H_2O$ and $[C_6H_2(NO_2)_3O]_2 Mn . 5H_2O$. But the two types merge into one another on the border line, and six new cases met with by the author belong to this intermediate type sensitive to variations of both temperature and wave-length.

They are rhombic rubidium sulphate, Rb_2SO_4, rhombic cæsium selenate, Cs_2SeO_4, monoclinic ammonium selenate, $(NH_4)_2SeO_4$, monoclinic cæsium magnesium sulphate and selenate, $Cs_2Mg(SO_4)_2 . 6H_2O$ and $Cs_2Mg(SeO_4)_2 . 6H_2O$, and the monoclinic form of an organic substance ethyl triphenyl-pyrrholone, the triclinic methyl analogue of which (both the ethyl and methyl compounds being dimorphous and exhibiting a triclinic variety) has already been referred to on pages 98 and 429. Ammonium magnesium chromate, $(NH_4)_2Mg(CrO_4)_2 . 6H_2O$, is a seventh of these intermediate cases which has been fully investigated by the author, but was discovered by Murmann in the year 1857. Cæsium selenate is a particularly interesting case, for within the limits of the ordinary temperature and 250° C. each of the three axes of the optical ellipsoid in turn becomes the first median line. The substance saccharine, $C_6H_{10}O_5$, is also one of these border-line cases remarkably sensitive to both kinds of physical change.

The following table expresses concisely the facts as regards the three definite substances chiefly sensitive to change of wave-length; the value of the apparent optic axial angle in air 2E is shown for Li, Na, and Tl-light, together with the direction of the plane of the optic axes.

[TABLE

Substances with Optic Axial Angles varying enormously with Change of Wave-length.

Light.	Brookite.		Picrate of Iron.		Picrate of Manganese.	
	2E.	Plane of Optic Axes.	2E.	Plane of Optic Axes.	2E.	Plane of Optic Axes.
Li	58° 0′	(001)	50° 16′	(100)	41° 53′	(100)
Na	38 10	(001)	24 48	(100)	15 30	(010)
Tl	21 40	(010)	46 54	(010)	57 13	(010)

In the case of brookite and iron picrate the uniaxial figure is exhibited for a wave-length between yellow Na-light and green Tl-light, in the former case in the neighbourhood of wave-length 0·00055, whereas in the case of manganese picrate the critical wave-length is between lithium and sodium light. A mixed solution containing specific proportions of the two picrates has been found to yield crystals showing the uniaxial cross and circular rings for sodium light.

Extremely interesting observations have been made by Brugnatelli [1] concerning saccharine, $C_6H_{10}O_5$, an optically active substance crystallising in the bisphenoidal (hemihedral) class of the rhombic system, like the triple tartrate of potassium, sodium, and ammonium, and the two double tartrates admixed in the latter. Saccharine is the lactone or anhydride of saccharic acid, $C_6H_{12}O_6$, and is obtained by the action of lime on a solution of invert sugar; it crystallises from a hot saturated solution in excellent large crystals of prismatic habit, which melt at 160°, and yield a dextro-rotatory solution. The crystals cleave readily along {010}, and the first median line is perpendicular to this cleavage face. The temperature at which the uniaxial figure is produced varies considerably in different crystals; while the average temperature observed by Brugnatelli was 15°, actual temperatures were 12°, 17°, and 26° for sodium light. The more perfect the crystal, however, the nearer to 15° was the temperature at which the uniaxial rings and cross were formed. A cleavage plate two millimetres thick from a magnificent clear crystal gave it at 15·8° for sodium light. For all wave-lengths between D and violet the optic axes lie in the plane {100}, whilst for light between D and the red end of the spectrum they lie in {001}. The temperatures at which the uniaxial figure was produced for the various wave-lengths with the plate just alluded to is shown in the following table:

[1] *Zeitschr. für Kryst.*, 1898, *29*, 54.

[Table

Light corresponding to Spectrum Line.	Temperature for Production of Uniaxial Figure.
B	6·6°
C	9·0
D	15·8
Caβ	21·3
Tl	23·8
E	26·0
b	27·4
F	34·7
Srδ	39·5
G	48·0

The results are also expressed in the accompanying curves in Fig. 771, of which the abscissæ are wave-lengths and the ordinates values of 2E. Separate curves are given for the temperatures 16°, 21°, and 26°. The values of 2E in the plane {100} are considered as

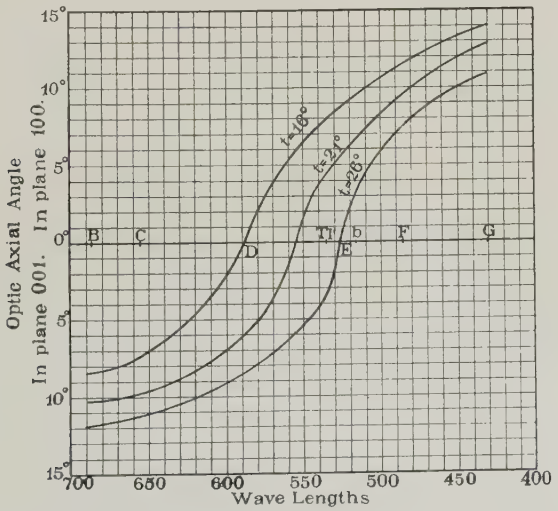


FIG. 771.—Optic-Axial-Angle Curves of Saccharine for the Temperatures 16°, 21°, and 26°.

positive, and those in {001} as negative. It is clearly obvious from this diagram that the curves are very steep in the neighbourhood of the critical zero angle of the optic axes, when the uniaxial figure is produced; that is to say, near the critical position of identity the optic axes move extraordinarily rapidly with change of wave-length. Also, the curves on the two sides of zero are unsymmetrical.

Pockels [1] has shown that the conditions for such a substance, the optic axial angle of which is very sensitive to change of wave-length, may be expressed by a formula. He starts with the well-known formula

[1] *Lehrbuch der Krystalloptik*, p. 71.

connecting 2E, the apparent angle in air, with the refractive indices α, β, γ, namely :

$$\sin E = \gamma \sqrt{\frac{\beta^2 - \alpha^2}{\gamma_2 - \alpha_2}} = \frac{\gamma}{\sqrt{\gamma^2 - \alpha^2}} \sqrt{\beta^2 - \alpha^2},$$

and replaces the refractive indices by their Cauchy dispersion formulæ of the type $A + \frac{B}{\lambda^2}$, thus obtaining the following differential equation as the expression of the change of the apparent optic axial angle with the wave-length λ :

$$\frac{dE}{d\lambda} \text{ or } \frac{d \sin E}{d\lambda} = -\frac{\gamma^2}{\gamma^2 - \alpha^2} (B_2 - B_1) \cdot \frac{1}{\sin E} \cdot \frac{1}{\lambda^3}.$$

From this formula it is apparent that when $E = 0$ the differential quotient $\frac{dE}{d\lambda}$ becomes infinite, and that in the neighbourhood of zero E must change very rapidly with λ ; also that the two parts of the curve for the two different sides of zero must be unsymmetrical, as is evident from the diagrams, because for equal values of E the change becomes the greater the smaller the wave-length.

A somewhat similar expression has been derived by S. Kreutz,[1] where g and h are the constants of the Cauchy formula ; it runs as follows :

$$\frac{d \tan V}{d\lambda} = -\frac{g}{g'} \frac{\left(h - \frac{h'}{g'}\right)}{\tan V \lambda^3}.$$

Both these formulæ of Pockels and of Kreutz agree in indicating that when a small optic axial angle becomes smaller it does so more rapidly than a larger angle, the existing dispersion becoming greater ; indeed, it becomes a maximum for E or $V = 0$. Moreover, the order of the dispersion comes into play, that is, whether it be $\rho > \upsilon$ or $\upsilon > \rho$. The shorter the wave-length, the more rapid the change, so that the optic axial angle diminishes more rapidly for blue light than for red. Hence, when the dispersion is $\rho > \upsilon$ and the angle is diminishing, both these influences (the approach to the zero angle and the energetic action of a short wave-length) co-operate to produce large change ; but if $\upsilon > \rho$, the effect is differential. The formulæ also show that large dispersion of the axes is to be expected when the double refraction is weak.

Thus the rules found by the author in the year 1894, purely from experiment, to apply in the case of rubidium sulphate, and which have since been amply confirmed by four other new examples among the sulphates and selenates of the alkalies and their double salts, as well as in the case of gypsum, have since been absolutely verified from the mathematical point of view by Pockels and Kreutz. We may now, therefore, inquire more in detail into some of the cases of sensitiveness to both change of

[1] *Ber. der kais. Akad. Wien*, 1908, *117*, 9.

wave-length and alteration of temperature, which have been investigated experimentally by the author, and which include the historic case of gypsum.

The case of the monoclinic variety of ethyl triphenylpyrrholone (for a description of the alkyl triphenylpyrrholones and their interesting isomorphism see Chapter LIV.) is very similar to that of rhombic brookite, the uniaxial cross and circular rings being exhibited for a wave-length in the slightly greenish yellow ; and as the substance is practically colourless (a very faint yellow only developing on keeping in the daylight), whereas brookite is deep red, the phenomena are not interfered with by absorption and are particularly brilliant. A crystal of the substance is represented in Fig. 772, and in Fig. 773 a reproduction is given of six drawings representing the interference figures, at *a* for red lithium light, at *b* for yellow sodium light, at *c* for slightly greenish-yellow light of the critical wave-length 0·000575 mm. for which the uniaxial figure is produced, at *d* for thallium light, at *e* for a mixture of sodium and thallium light, and at *f* for white light. The last figure reminds one forcibly of the figure afforded by brookite in white light. Employing the spectroscopic monochromatic illuminator described in Chapter XLIV., as shown in Fig. 715, an instrument which the author devised later than his memoir on the triphenylpyrrholones, the changes of the optic axial figure can be followed in a very complete and beautiful manner, and the exact wave-length in the greenish yellow can be readily determined for which the uniaxial figure is produced. The value given, 0·000575 mm. has been recently obtained (April 1920) with two of the original crystals, the two results being identical. A section-plate at least a millimetre thick is required to afford a sharp series of interference figures, on account of the very feeble double refraction, which is the cause of the extreme sensitiveness to change of wave-length of the illuminating light.

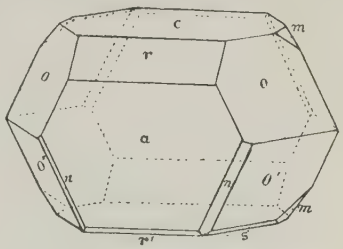


FIG. 772.—A Crystal of Monoclinic Ethyl Triphenylpyrrholone.

Rubidium sulphate is the central member of the series of three isomorphous rhombic sulphates of potassium, rubidium, and cæsium (K_2SO_4, Rb_2SO_4, Cs_2SO_4). This series affords one of the clearest instances of "eutropic" or family-group isomorphism, which are cases of the strictest type of isomorphism governed by the general law that the crystallographic properties are functions of the atomic weights or atomic numbers of the interchangeable elements (here potassium, rubidium, and cæsium) of the same family group which give rise to the series (see page 383). Now the double refraction is already low in the first member of the series, potassium sulphate, and this particular property obeys the law just referred to in the sense of diminution, so that the extreme refractive indices α and γ converge towards equality as the atoms of potassium are replaced by the heavier ones of rubidium and the still heavier atoms of cæsium. This is shown graphically by the curves in Fig. 774, which represent the

reciprocals of the three refractive indices, the axes of the Fresnel ellipsoid, for the three salts, the lengths of these ellipsoidal axes being taken as abscissæ and the atomic weights of the alkali metals as ordinates. The dotted curves express the total change in the axial lengths of the ellipsoid, while the continuous curves represent the relative values of the three

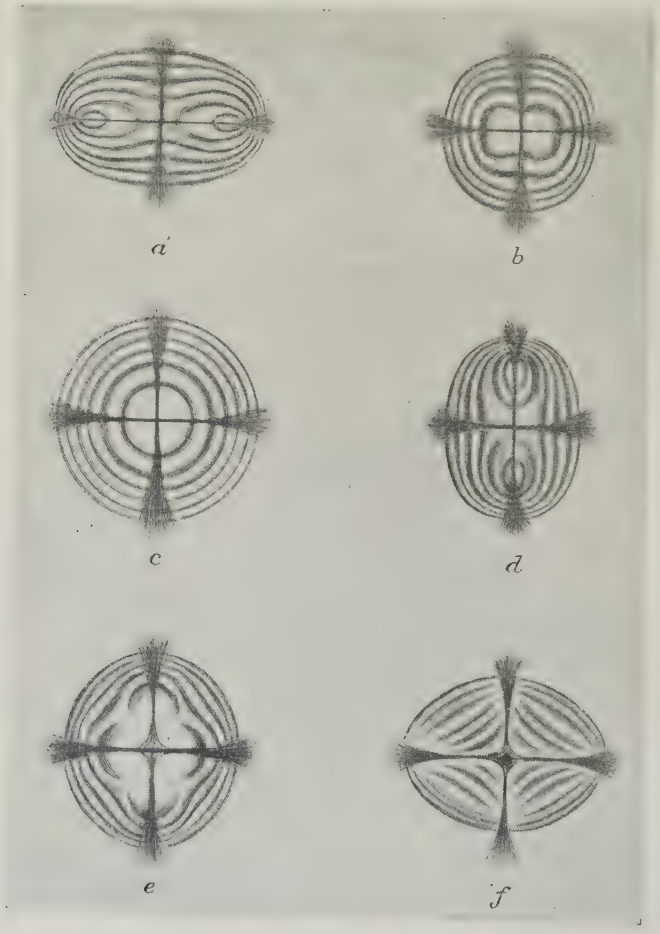


FIG. 773.—Interference Figures of Monoclinic Ethyl Triphenylpyrrholone.

axes for each salt, when the *b*-value is taken as unity. So rapid is the convergence that the *a* and *c* curves (these letters representing the crystallographic axes, identical in direction in these rhombic salts with the axes of the optical ellipsoid) intersect before the rubidium salt is reached, and the *b* and *c* curves do so almost exactly at the rubidium salt, so that the double refraction, represented in the case of potassium sulphate by the distance between *b* and *c*, is reduced in rubidium sulphate to the smaller

amount indicated by the distance between the a and b curves. As, however, besides very small double refraction we have also the condition of nearness of two of the refractive indices, those corresponding to the directions of the crystallographic axes b and c, the conditions are ideal for the exhibition of large dispersion of the optic axes even at the ordinary temperature, and for the possibility of crossing of the optic axial planes at a somewhat elevated temperature. On heating the section-plate perpendicular to the first median line, rise of temperature is observed fortunately to act in the right direction, in the way of further reduction of the optic axial angle, so that at 40° the uniaxial figure is produced for

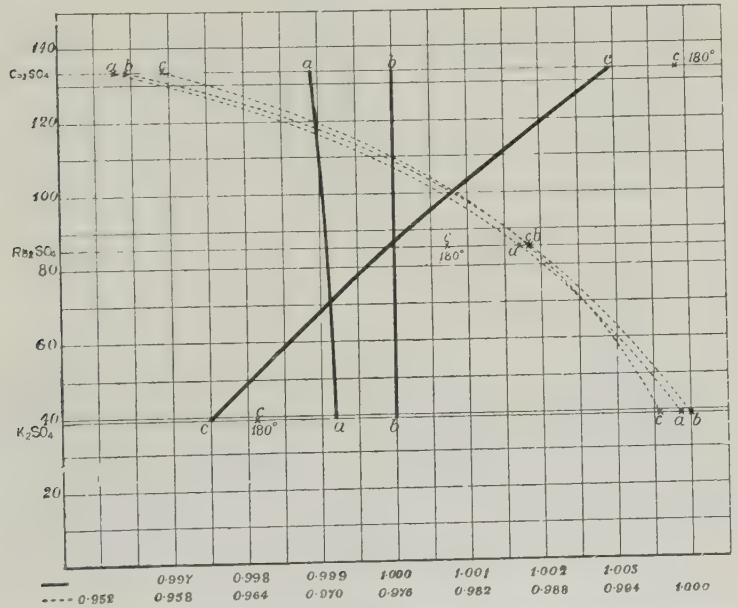


FIG. 774.—Curves of Axial Values of the Fresnel Ellipsoid for the Sulphates of Potassium, Rubidium, and Cæsium.

red lithium light, and at succeeding higher temperatures for the other wave-lengths in their order, until it is finally formed at 65° for G-violet light.

Cæsium selenate, Cs_2SeO_4, the third member of the analogous group belonging to the same rhombic series of eutropically isomorphous selenates, behaves similarly, and the curves for this group exhibiting the fact are shown in Fig. 775. In this case, for the sake of variety, the relative values of the axes of the optical indicatrix are portrayed, which represent the refractive indices directly. The reduction of the double refraction according to the law in this group only results in equality of two of the indices being reached about the position of the cæsium salt, the c-value (γ index) coming to equality with the a-value (β index) just before arrival at cæsium selenate, the two curves crossing, and the

c-value being brought inside the a and b values as the now intermediate index β, while the a-value corresponds henceforth to γ.

The double refraction, represented by the distance between a and b, is now enormously less than it was in the potassium salt, represented by the distances between b and c for that salt, and so one of the conditions for large dispersion of the optic axes is brought about.

The first effect of heat on the section-plate perpendicular to the first median line, the axis b, brings the c-curve still further inside the a-curve, so that it passes the intermediate position between a and b, the optic axial angle increasing to 90°, and the optic axial brushes subsequently passing out of the field of view; the c-curve then approaches the b-curve, with diminution of the optic axial angle about

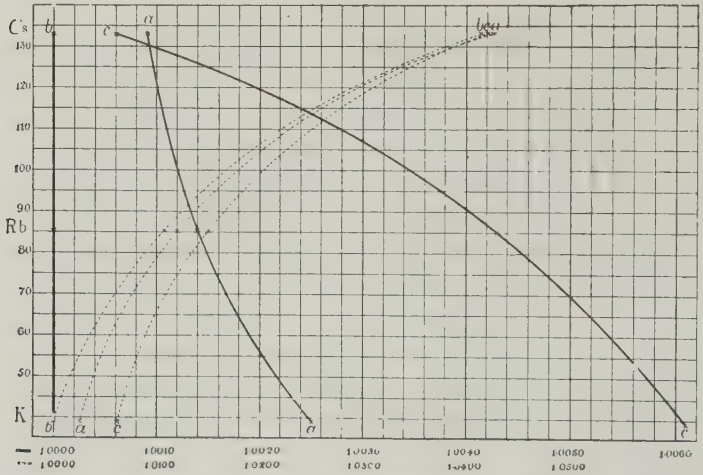
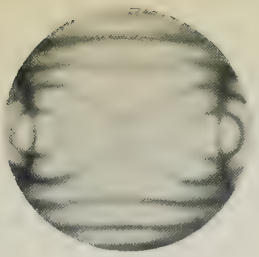


FIG. 775.—Curves of Axial Values of the Optical Indicatrix for the Selenates of Potassium, Rubidium, and Cæsium.

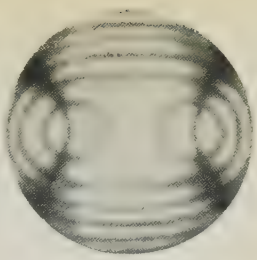
a new acute bisectrix, the axis a, which had formerly been the second median line, the double refraction having also changed from negative to positive; this occurs so rapidly, moreover, that if a second section-plate perpendicular to this new acute bisectrix a, be adjusted on the polariscopical goniometer and similarly heated, it is observed that at 92° to 98° for the different wave-lengths of light from red to blue the c-curve actually intersects the b-curve, the uniaxial cross and rings being produced as this occurs for these different wave-lengths in succession. Continuing the heating, the optic axes then again bifurcate, but along a new diameter at right angles to the old one, corresponding to the crossing of the optic axial planes, and they separate more and more until they disappear out of the field of the polariscope. If now a plate be ground perpendicular to a third bisectrix, the axis c, and heated to 150°, the optic axial rings become visible on opposite sides of the extreme edge of the field, and approach each other about this new

SERIES 1. ORDINARY TEMPERATURE.

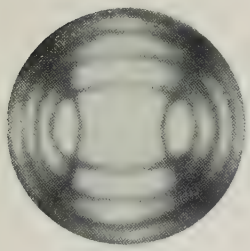


For Li-light.

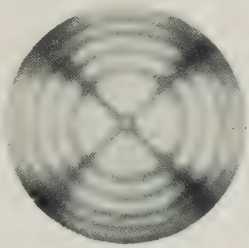
For Na-light.



For Tl-light.



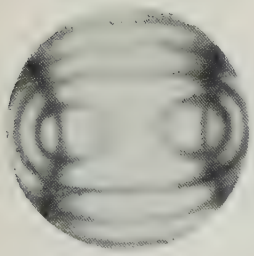
For F-light.



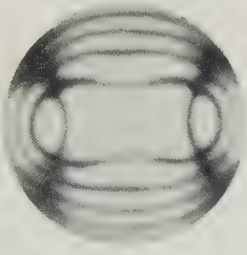
For Wave-length 466.

For G-light.

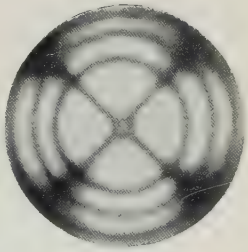
SERIES 2. TEMPERATURE 78°.



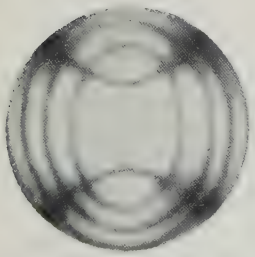
For Li-light.



For C-light.

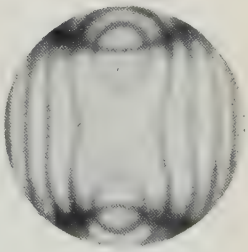


For Na-light.



For Tl-light.

For F-light.



For Wave-length 466.

FIG. 776.—INTERFERENCE FIGURES OF CÆSIUM MAGNESIUM SELENATE.

Plate to face page 1066.

bisectrix, until at 250°, when the heating has to cease for obvious reasons, the angle has become less than 90° and another change of sign of double refraction has occurred, from positive back again to negative, as it is at the ordinary temperature, and the angle is still becoming less moment by moment. Thus this unique substance has for its first median line within the comparatively short range of 250° of temperature every one of the three axes of the optical ellipsoid in turn.

The double sulphate and double selenate of cæsium and magnesium afford two cases in which the uniaxial figure is produced at the ordinary temperature, for a wave-length in the blue, 0·000450 and 0·000466 millimetre in the two respective cases. The interference figures of cæsium magnesium selenate, for six wave-lengths at the ordinary temperature and at 78°, are illustrated in the photographic reproductions given in Fig. 776, Plate VI. It will be clear that the optic axes are well separated in the horizontal plane at the ordinary temperature for red lithium light, and that they approach each other more and more as the wave-length is diminished, through Na-light, Tl-light, and F-light, until for the critical wave-length 0·000466 the uniaxial cross and circular rings are formed. Subsequently, as the violet is approached, the optic axes separate again, more and more, but along the vertical diameter, as illustrated by the figure for G-light. On heating the section-plate the uniaxial figure travels through the spectrum towards the red for successive higher temperatures, and the other six figures represent the conditions at 78°, for which the crossing of the axial planes occurs for sodium light, the uniaxial figure being produced; the optic axes are then separated in the horizontal plane for wave-lengths on the red side, and in the vertical plane for wave-lengths on the blue side. By the time the temperature of 97° is reached, the optic axes for all wave-lengths are separated in the vertical plane, at a small angle for red, and at greater and greater angles towards the blue.

The illustrations are actual photographs of the figures observed. The section-plate requires to be half a centimetre thick in order to exhibit such sharp figures, an emphatic illustration of the necessary condition of low double refraction for the production of crossed-axial-plane dispersion.

Ammonium magnesium chromate exhibits the uniaxial figure at the ordinary temperature for wave-length 0·000664 mm. in the red of the spectrum. The axes are separated in a plane perpendicular to the symmetry plane $16\frac{1}{2}°$ for the extreme red, and in the symmetry plane itself 78° for green cadmium light, as seen in air. On heating the crystal the uniaxial cross is formed for successively shorter wave-lengths as the temperature rises; thus at 50° C. it is produced for wave-length 0·000636 mm. in the orange.

The Case of Gypsum. The Mitscherlich Experiment and Apparatus for its Projection.—It has been shown in Chapter XLII., page 928, that at the ordinary temperature the optic axes of gypsum, $CaSO_4 . 2H_2O$, lie in the symmetry plane of the monoclinic crystals, the inclined dispersion being strongly marked. The first median line lies in the obtuse

angle of the axes a and c, and is inclined 37° 42′ to the normal to $a=(100)$ and 46° 40′ to the axis a; also 52° 18′ to the axis c and 43° 20′ to the normal to $c=(001)$, as clearly shown in Fig. 777.

The true optic axial angle $2V_a$ at 10°, and the apparent angle in air 2E at 11·5°, are given for seven wave-lengths in the following table:

Values of True and Apparent Optic Axial Angles of Gypsum.

	$2V_a$ at 10° C.	2E at 11·5° C.
For Li-light	60° 27′	99° 16′
„ C „	60 31	99 27
„ Na „	61 1	100 36
For wave-length 0·000573 .	61 4	100 43
For Tl-light	60 51	100 34
„ F „	60 34	99 58
„ G „	59 48	98 24

One of the most remarkable things about gypsum is that the optic axial angle does not go on steadily increasing or diminishing with the regular progression of wave-length, but that when a certain wave-length in the greenish yellow is reached, 0·000573 millimetre, the progress is arrested and the angle begins to alter in the opposite sense, in other words, the optic axial angle has a maximum for wave-length 0·000573.

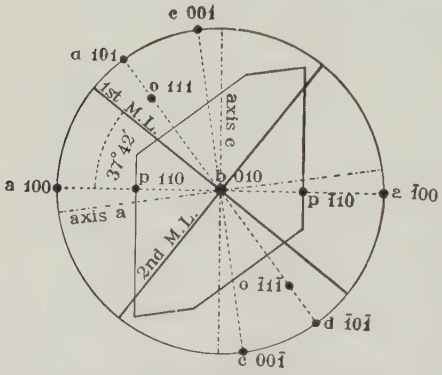


Fig. 777.—Positions of the Bisectrices of the Acute and Obtuse Optic Axial Angles of Gypsum.

On heating the section-plate the optic axes move towards one another and the centre of the field, and at a temperature of about 91° C. coalesce in the centre to produce the uniaxial cross and circles. The table on page 1070 shows the exact corrected temperatures at which this occurs for the different parts of the spectrum.

A considerable amount of difficulty has attended the exact determination of these temperatures. A first attempt,[1] using the apparatus shown in Fig. 761, page 1042, afforded results which were obviously too high, just over the temperature of boiling water; whereas a crystal immersed in boiling water and then transferred rapidly to the polariscope shows the crossing already accomplished. The source of error was the considerable correction rendered necessary by the conduction of heat away from the crystal section-plate by the metallic crystal-holder, and the fact that

[1] Tutton, "The Optical Constants of Gypsum at Different Temperatures," *Proc. Roy. Soc.*, A, 1908, *81*, 40.

the temperature of the crystal, therefore, never attained that of the air-bath in which the heating occurred. Determinations of the correction, by use of a miniature thermometer with bulb occupying the place of the crystal, after reducing conduction to a minimum by using a crystal-holder of boxwood and platinum, as described on page 1044, proved inadequate for temperatures above 70°.

But complete success, due to the device by Dr. A. Hutchinson of an ingenious little apparatus for immersing the crystal in a liquid during the experiments, eventually attended further efforts to avoid this source of error.[1]

A small shallow circular brass cell, provided with a glass top and bottom, was constructed and fitted with two brass tubes, one on each side, to act as inlet and outlet for a stream of water—saturated with calcium sulphate, in order to minimise any solvent action on the crystal, and heated

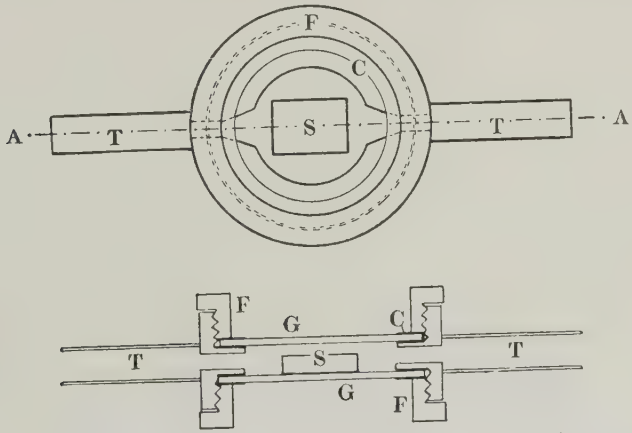


FIG. 778.—Hot-water Cell for heating Gypsum Plate on Stage of Microscope.

to any required temperature below 100°—which was conducted through the cell during the observations. The temperature of this stream of aqueous solution of calcium sulphate was taken immediately before entering and directly after leaving the cell by two thermometers graduated to $\frac{1}{5}$° C. The thermometers were enclosed in the glass tubes by which the hot solution was conducted to and from the cell, and were therefore wholly immersed in the hot liquid. They were compared with the standards at the National Physical Laboratory, and the corrections found necessary duly applied.

The construction of the cell is indicated in Fig. 778, the upper portion being a plan, and the lower a vertical section through the line AA, both full size. The top and bottom of the cell are formed by the glass plates G, which are held in position by the screw flanges F. Rings of thin cardboard below the glass keep the cell water-tight, and thin brass washers

[1] Hutchinson and Tutton, "On the Temperature of Uniaxiality in Gypsum," *Mineralog. Mag.*, 1912, *16*, 257.

C protect the glass plates from the direct action of the screws. The hot liquid enters and leaves the cell by the tubes TT, to which horizontal glass tubes about 1 cm. in internal diameter are connected. These contain the thermometers, which are arranged with their bulbs as near the cell as possible. The section-plate of gypsum perpendicular to the first median line, seen at S, is held in position by a small spring (not shown) formed by a coil of thin brass wire.

The cell was adjusted on the stage of the Dick polarising microscope (see Fig. 821, Chapter LII.), and was insulated from the stage of the microscope and protected from radiation by suitable coatings of cardboard and cotton-wool. The tubes containing the thermometers were also protected for the greater part of their length. On allowing the hot calcium sulphate solution, kept stirred in a large copper tank, to run through the cell it was found that the temperature of uniaxiality, as measured by the thermometers immersed in the stream, could easily be kept steady for a time sufficiently prolonged for the changes produced by alteration of the wave-length of the illuminating light to be accurately studied. Occasionally the temperatures indicated by the two thermometers were the same, but usually that first reached by the stream read a little higher than the other. The difference did not, however, generally exceed $\frac{1}{2}°$, and the mean value of the two readings was taken as giving the actual temperature of the section-plate in the cell.

The results obtained on different days and with two different section-plates proved to be very concordant, and are embodied in the following table:

λ.		
0·000434 mm.	For G-light cross and rings produced at	88·1° C.
486	„ F „ „ „	90·1
535	„ Tl „ „ „	90·8
573	Last wave-length (0·000573) for which uniaxial figure is produced	91·0
589	For Na-light cross and rings produced at	90·9
656	„ C „ „ „	90·4
671	„ Li „ „ „	90·2

After the production of the cross for the particular wave-length of the illuminating light the axes separate along that diameter of the field which is perpendicular to the original direction of separation, the plane of the axes now changing to one at right angles to the symmetry plane. Between the ordinary temperature and 91° also, as shown in Chapter XLII. (p. 927), the first median line itself moves $5\frac{1}{2}°$ in the symmetry plane, towards the axis *c*. These phenomena of gypsum were demonstrated by Mitscherlich to the Berlin Academy in the year 1826, and their exhibition has since been referred to as the "Mitscherlich experiment." The usual mode of performing this experiment with the lantern polariscope has hitherto been to place a somewhat large section-plate of gypsum, cut perpendicularly to the acute bisectrix of the optic axial angle, in a metal frame having a projecting part which can be heated by a spirit lamp or small Bunsen flame. But the author has demonstrated to the Royal

Society,[1] and also to the British Association at the 1909 meeting at Winnipeg,[2] a much more elegant mode of performing this beautiful experiment, without any extraneous heating whatsoever. The improved form of lantern polariscope was employed which, as regards its arrangement for parallel light projection, has already been described in Chapter XL. and illustrated in Fig. 633, page 853. Its arrangement for projections in convergent light, including the Mitscherlich experiment, is shown in Fig. 779. The convergent lens-system is such as concentrates the light rays so perfectly in the centre of the crystal, on a spot not exceeding a couple of millimetres in diameter, that the heat rays simultaneously thus also concentrated are quite adequate to effect the crossing of the optic axial plane. This is true, moreover, even although the greater proportion of the heat rays are removed by the water cell, which is always essential in order to protect the balsam of the very valuable large Nicol prisms from softening. There is no necessity for the crystal to be much larger than this focal spot, so the author employs a plate, any one of several prepared by Messrs. Steeg & Reuter of Homburg, which is only 6 millimetres square, but 2 millimetres thick in order to ensure a sharp interference figure (the double refraction being so low), mounted in a miniature blackened thin sheet-brass or better platinum-foil carrier-frame with circular aperture 3 millimetres in diameter on each side, through which the light enters from the convergent system of lenses and leaves to enter the similar collecting system. The little frame itself, only 7 by 6 by 3 millimetres, has a lip-like continuation on one side, which serves for gripping by the crystal-holder; it is held directly by a hard-wood holder, to prevent loss of heat by conduction, and which in turn is gripped by the ordinary metallic pincette of the crystal-adjusting apparatus.

The disposition of the apparatus for the performance of the Mitscherlich experiment is that shown in Fig. 779. The electric lantern is provided with a 4½-inch double condenser, and an adjusting table for the electric arc furnished with three rectangular adjusting movements, which are particularly useful, indeed, imperative in this experiment; the electric lamp is a Brockie-Pell self-feeding one, but an improved Oliver lamp does equally well. The water-cell of 2 inches thickness may be supported in front of the lantern-slide frame, as in Fig. 633, or, as now shown in Fig. 779, separately on an adjustable holder with semicircular stirrup, as the first of the fittings on the hard mahogany guiding bed on which the various accessories are mounted. After trying both this and the lathe-bed method of mounting the parts of the apparatus the author now prefers the hard mahogany bed fitted with rigid and very true rabbets, which latter can be cut away for about 4 inches to the right of the centre near the analyser in order to afford a place for the removal or interchange of the various supporting stands carrying lenses or other fittings without having to remove the large Nicols. All the bases of the supports (seen better in the case of the parallel-light fittings also shown, in the recess underneath, in Fig. 779), whether as narrow as 1½ inch or broader, are partially cut away underneath and packed with smooth felt to facilitate sliding, and are also fitted with a couple of fixing screws, passing through the little fixed transverse dovetailed brass guiding bed for the bevelled slider which directly carries the column, and which enables the transverse adjustment to be carried out.

[1] *Proc. Roy. Soc.*, A, 1908, *81*, 41.

[2] *Brit. Assoc. Reports*, Winnipeg Meeting, 1909, First Evening Discourse.

After the water-cell comes the large polarising Nicol, already fully described in Chapter XL., with its convexo-concave parallelising lens at the end nearest the

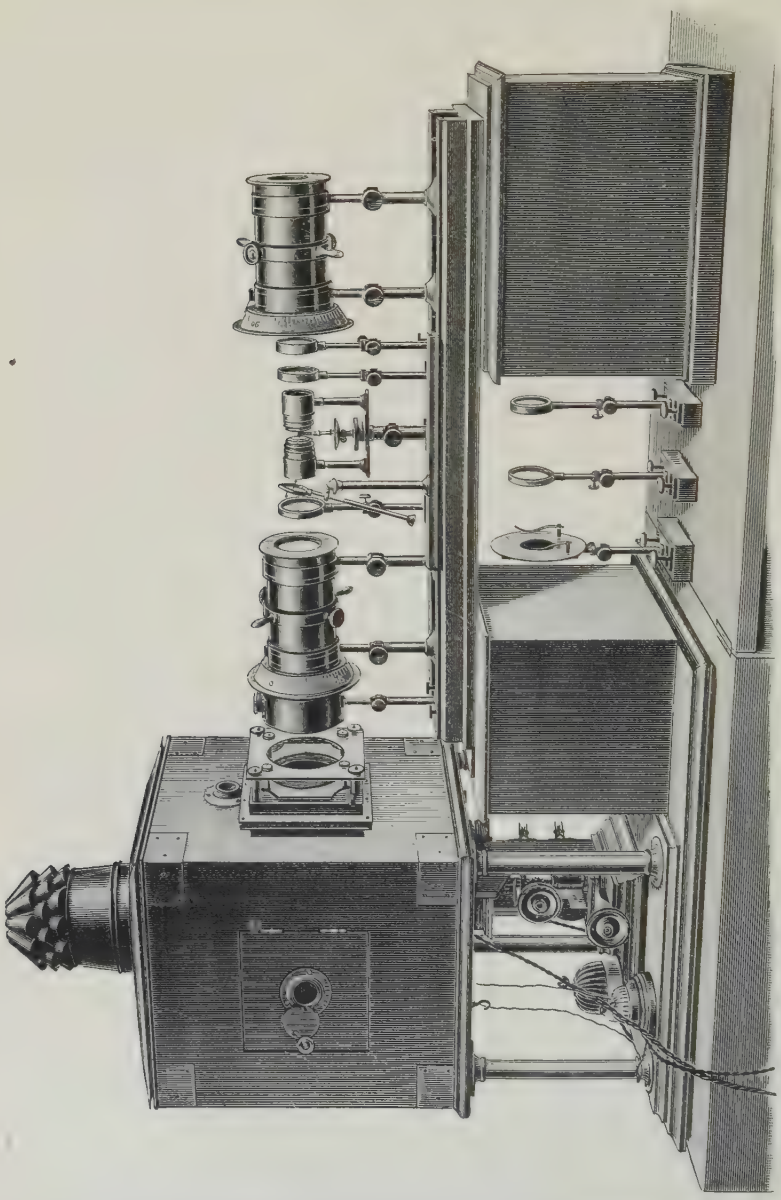


FIG. 779.—Projection Polariscope arranged for the Mitscherlich Experiment and other Projections in Convergent Polarised Light.

water-cell, the light being so converged upon this lens by adjustment of the distance of the electric arc from the condenser of the lantern that the rays leaving the lens are rendered strictly parallel, and pass as such through the polariser. Besides the

main plinth guiding bed, and fixed along the middle part of its front rabbet, there is a subsidiary metallic dovetailed bed, in which moves a bevelled slider carrying a columnar tube with inner rod adjustable for length, and terminating in a ball-and-socket universal joint, which carries at its summit a very convenient clip-holder for the cork or other mounts of section-plates of crystals or other objects which it is desired to introduce into the path of the rays. In the Mitscherlich experiment illustrated in Fig. 779 it is not used, being rotated away in front from the path of the light rays.

The convergent light arrangements after the polariser are as follows. First comes an independently mounted 5- or 6-inch plano-convex lens (the two alternatives being both provided) to commence the convergence of the light rays. Then follows the optic-axial-angle goniometer, with its two exactly similar but inverted systems each of four plano-convex lenses of very short focus, of which only three are usually employed, the outer smallest one in each case being only attached when extremely strong convergence is required. The largest of the battery of lenses, all the individuals of which are separately mounted and readily detachable by unscrewing the mounts, in each case is screwed into a short tube, which slides in an outer one supported by a column rising from an elongated metallic plate. This base-plate bearing the two columns is pierced at the centre by, and rigidly attached to and carried by, a stout tubular axis, adjustable for height as an inner tube within a strong outer column rising from a transverse slider in a dovetailed metallic bed, screwed on to a mahogany slider in the main guiding bed similar to the others but much broader, having more to carry. The two convergent systems are thus supported by the two columns rising from the plate in such a manner that each can be independently approached to or drawn away from the central space between them, where the crystal-plate is held at the head of an adjusting and centring arrangement of the kind provided with the von Groth universal apparatus (Fig. 762, page 1045). The central boss of this adjustable crystal-holder is not mounted directly at the head of the tubular sliding column, but to a second inner sliding and rotating short tube, which carries a radial pointer forming an indicator of the rotation of the crystal-axis about a silver divided circle fixed above the elongated cross-plate and concentrically around the tubular support. The central axis of the crystal-adjusting apparatus passes freely down through both these supporting tubes and the still narrower tube of the adjusting apparatus, and is adjustable with fixation for height so as to bring the crystal absolutely to the common focus of the convergent systems. Transverse and longitudinal adjustments and a universal circular motion are also afforded by the centring and adjusting apparatus, so that the crystal is adjustable in all directions, and the whole arrangement is an absolutely symmetrical one.

After this very convenient form of projection optic-axial-angle goniometer comes a doubly convex field lens of $2\frac{1}{4}$ inches focus on its adjustable pedestal, and this is closely followed by an achromatic lens combination of $6\frac{1}{4}$ inches focus likewise independently mounted, which acts as a most efficient projecting lens for the focussing of the interference figures in convergent polarised light on the screen. Finally comes the large analysing Nicol. As now described this arrangement is of general application for the projection of the rings and brushes of crystals, and for any other purposes for which convergent polarised light is required.

To perform the Mitscherlich experiment, the little crystal in its miniature platinum-foil frame is supported in the wooden holder, which grips the lip of the frame, and the wooden holder is held in turn by the ordinary pincette of the adjusting apparatus, and the crystal adjusted to the centre of the space between the convergent systems in such a manner that the clear aperture of the crystal is at the approximate common focus of the latter. The planes of the Nicols are arranged at 45° left and right

respectively of the vertical zero line, being thus crossed for the production of the dark field. The electric arc is then switched on, preferably by a switch on the lantern itself, and if the lenses and the crystal are correctly adjusted the focal spot of light will be seen to be impinged right on the centre of the 3 millimetres of clear aperture of the crystal, which is thus brilliantly illuminated. On regarding the screen, if the crystal-plate has been arranged correctly as regards its orientation, which will have been attended to in mounting in the platinum frame, the two systems of optic axial rings will be observed almost at once to appear at the right and left margins of the field, and to be visibly moving towards the centre. A little centring of the light will now generally be necessary by means of the large milled heads of the three rectangular movements of the adjusting table of the electric lamp, in order to ensure even, well-centred, and brilliant illumination of the field. The axial brushes themselves soon become visible, as reproduced in Fig. 780 of Plate VII., and march rapidly with the rings towards the centre of the field, as indicated by the next photograph, Fig. 781, where brilliant colours begin to break out, constantly changing and giving place to others, as first looped spectrum-lemniscates and subsequently ellipse-like ones appear round the brushes. The last complete ring round each of the two brushes finally opens out, the two rings becoming first a loop (∞-shaped) lemniscate, then an apparent ellipse enveloping both brush-vertices, and lastly a true circle, surrounded by five or six others, all in spectrum colours, and the brushes themselves coalesce to form a black uniaxial St. Andrew's cross, as shown in Fig. 782.

In order to effect the changes steadily and without hesitation the light must be kept well centred, so that the focal spot is concentrated always on the crystal. The cross and circular rings soon break up again into hyperbolæ and lemniscates, at first of the ellipse-like character, but afterwards forming loops and then complete rings round the two separated axes, as shown in the fourth photograph, Fig. 783 ; the vertices of the hyperbolæ are now, however, separated along the vertical diameter of the field, and when they are well asunder the experiment should be stopped, as gypsum loses its water of crystallisation slightly above 120°. It is only necessary to blow a gentle stream of air across the crystal, however, or to introduce a glass plate a little obliquely somewhere in the optical train between the lantern and the crystal, to cause the figure to recede again to the crossing point and beyond it, owing to the reduction of the temperature of the crystal by the cool air or the deflection of the focussed rays. Or an opaque screen may be intermittently introduced into their path before reaching the crystal, to effect the same purpose.

That the temperature for production of the uniaxial figure with gypsum is lower than that of boiling water may be readily demonstrated with the aid of a special little cell, rectangular outside and semicircular within. It is like that marked a on the little adjustable table y at the base of the larger optic-axial-angle goniometer, Fig. 759 on page 1040, but the middle part semicircularly cut out to form the ends and bottom of the cell is not quite so thick and is of hard boxwood instead of thick glass, in order

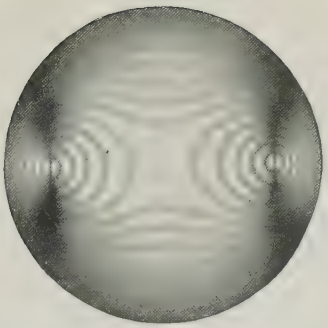


FIG. 780.—The Interference Figure just after commencement of warming. Temperature about 40° C.

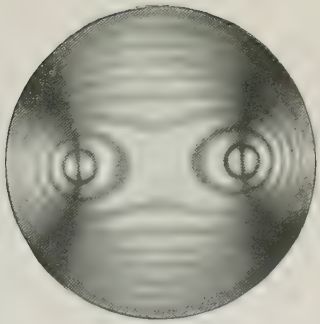


FIG. 781.—The Figure about a Minute later, the Optic Axes approaching the Centre. Temperature about 75° C.

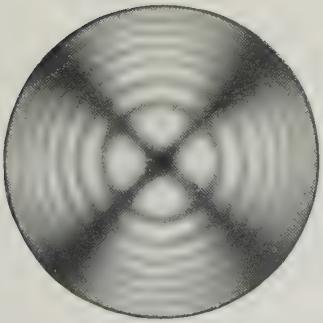


FIG. 782.—The two Optic Axes coincident in the Centre, two or three minutes from commencement of warming. Temperature 91° C.

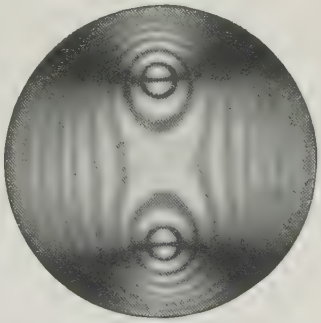


FIG. 783.—The Optic Axes reseparated in the Vertical Plane a minute or two later. Temperature about 115° C.

THE MITSCHERLICH EXPERIMENT WITH GYPSUM

Four Stages in the Transformation of the Interference Figure in Convergent Polarised Light on Heating to 115° C.

to withstand the hot water; the sides, as in case of the cell a, are of thin optically worked glass, or better still of fused quartz, cemented to the wood, with a hard balsam, or other cement, capable of withstanding 100° C. and insoluble in water. A small gripper for the lip of the little frame-mount of the crystal is fixed upright at the centre of the semicircular bottom of the cell, with the crystal adjusted once for all at the centre of the cell to afford a symmetrical interference picture on the screen.

The experiment may then be performed by pouring boiling water directly into the cell, when the interference figure will appear at once on the screen, and the crossing of the axes occurs very rapidly, the figure remaining constant for a minute or two when the axes have again separated —this time vertically. A better result still is obtained if the hot water be siphoned out and immediately replaced by a fresh supply from water on the boil. The most beautiful and regular effects occur, however, during the slow cooling of the water, the vertically separated brushes coming together and coalescing to form the rectangular cross as the temperature becomes reduced to 91°, and spreading out again horizontally more and more, as the cooling proceeds below this critical temperature, the colour changes with the lemniscates affording one of the most beautiful displays ever observed.

After satisfactorily verifying the truth of the production of the uniaxial figure below 100° C. by the use of pure water, subsequent experiments may be made with the water saturated with calcium sulphate (which only dissolves to a very slight extent), as there is then less danger of action on the polished surfaces of the gypsum crystal-plate.

The Case of Glauberite.—The double sulphate of sodium and calcium $Na_2Ca(SO_4)_2$, which occurs in natural crystals as the mineral glauberite, and which, like gypsum, crystallises in the monoclinic system, class 5 (holohedral prismatic), has also long been known to possess an optic axial angle which is very sensitive to change of temperature, combined with considerable dispersion of the optic axes. Brewster, so long ago as 1829, observed the fact, and it was studied in some detail by Laspeyres [1] in 1877. He showed that the morphological constants are:

$$a : b : c = 1{\cdot}2209 : 1 : 1{\cdot}0270\,;\quad \beta = 112°\ 10'.$$

He also found the double refraction of negative sign, the first median line (acute bisectrix) lying in the symmetry plane {010}, at 30° 46′ from the vertical axis c for sodium light; and that the plane of the optic axes is at right angles to the symmetry plane for all temperatures below that at which the optic axes cross and form the uniaxial figure, so that the dispersion of the optic axes at these temperatures is of the horizontal character, while for temperatures above that of apparent uniaxiality the plane of the optic axes is parallel to the symmetry plane, affording inclined dispersion. At the ordinary temperature of 18°, Laspeyres found the angle in air 2E to be 14° for red lithium light, 11° for yellow sodium light, and 8° for green thallium light, while for blue light the angle is zero, and the uniaxial figure is produced, even at this ordinary temperature

[1] *Zeitschr. für Kryst.*, 1877, *1*, 529.

of 18°. On raising the temperature the axes close in towards one another for light of any colour other than the blue and violet, until they coincide with production of the uniaxial cross and rings at some particular temperature, after which continued heating causes them to rediverge, but along the symmetry plane at right angles to their former direction of separation.

As regards the actual temperatures given by Laspeyres, they were determined with the air-bath of the Groth universal apparatus (Fig. 762 on page 1045), and for the reasons already stated are subject to considerable error unless a large and more or less uncertain correction is applied. The correct temperatures for production of the uniaxial figure for sodium and lithium light have, however, been more recently determined by E. H. Kraus,[1] by use of an oil bath in connection with the Fuess optic-axial-angle apparatus, the air bath of which was converted for the purpose into an oil bath by filling it with paraffin oil, of refractive index for sodium light 1·4702. The following were the results :

Temperature.	$2H_a$ (for paraffin oil).	
	Li-light.	Na-light.
18° C.	10° 12′	8° 28′
30	8 35	6 30
42·9	6 55	Uniaxial
51·8	Uniaxial	5° 37′
60	5° 42′	7 5
70	7 33	8 19
80	8 48	9 43
90	9 52	10 48
100	11 8	12 3

The temperature for uniaxiality, which is the ordinary (18°) for blue light, is thus shown to become higher with increase in wave-length of the light, being 42°·9 for yellow sodium light and 51°·8 for red lithium light. Both optic axes move equally with the temperature below the crossing point (the dispersion being horizontal), and unequally for temperatures beyond those for uniaxiality (the dispersion then becoming inclined).

Experimental Confirmation of Conditions for Crossed-axial-plane Dispersion.—In order to confirm the truth of the conditions for crossed-axial-plane dispersion laid down at the beginning of this chapter, the author has determined the refractive indices of all the substances referred to which exhibit the property, at not only the ordinary but the higher temperatures, and the phenomena observed have in all cases been both highly interesting and exactly in accordance with the conditions stated. In every instance when the 60°-prism affording the two indices of refraction which are supposed to become identical—at the temperature for which the section-plate perpendicular to the first median line shows

[1] *Zeitschr. für Kryst.*, 1913, *52*, 321.

the uniaxial figure—was heated to that temperature, the two large and brilliantly illuminated coloured images of the Websky signal-slit in the monochromatic light employed were seen steadily to approach one another, until at the exact temperature corresponding to the production of the cross and circular rings for that same wave-length of light which was illuminating the slit, the two images appeared identical; after this, when the temperature was still increased, or the wave-length was varied in the right direction by rotation of the prism circle of the monochromatic illuminator, they separated again on the other side of each other. When apparently identical, they were seen to be still two images, but overlapping; for no apparent extinction occurred when the Nicol prism carried in front of the eyepiece was rotated, one image waxing equally as the other waned (modified slightly by the fact that the 90° image, corresponding to light vibrating parallel to the refracting edge of the prism, is always slightly the weaker, owing to such light as is polarised and lost by reflection vibrating parallel also to the edge). The moment they were just separated again

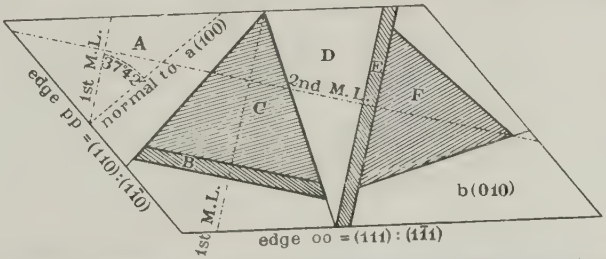


FIG. 784.—Plan on which Complementary Pairs of Plates and Prisms were cut out of the same Crystal of Gypsum, in order to afford all the Optical Constants.

one was extinguished by the Nicol placed at its 0°-position, while the other was extinguished when the Nicol was arranged at its 90°-position.

In the case of gypsum, in order to avoid any error due to slight differences between different crystals, two section-plates (B and E in Fig. 784) perpendicular to the first and second median lines respectively, with which measurements of optic-axial angle were made, and a complementary pair of 60°-prisms (C and F in the figure) affording all three refractive indices between them, were cut and polished for the author by Hilger, with truly worked plane surfaces, from a single large and highly perfect crystal, one complete set of optical constants being thus derived from one and the same crystal. The plan on which the crystal was cut will be clear from Fig. 784, the crystal lying on a clino-pinakoid face $b = \{010\}$, parallel to the symmetry plane. The prism C afforded the indices β and γ, while F gave α and β. It was with this latter prism that the observation of the approach to equality of two of the indices, in the case of gypsum α and β, with rise of temperature, was made, and their subsequent attainment of identity and then their passage past each other, followed, all of which occurred precisely in accordance with expectation derived from the optic-axial-angle phenomena afforded by the plate B perpendicular to the first median line.

For it was found that on slowly and very carefully heating this large and valuable prism giving α and β the two images of the collimator-slit gradually approached one another. Using sodium-light their separate existence could still be detected at 89° C., but at 91° they coalesced completely. When, however, the temperature had risen to 93° two independent images could once more be recognised.

Thus the conditions specified in the opening of this chapter as necessary for the production of crossed-axial-plane dispersion of the optic axes have been absolutely verified experimentally.

A complete set of refractive index determinations was carried out with this very fine pair of gypsum prisms, and for each of three temperatures, namely, the ordinary (12° at the time), 98°, and 105°. The results are given below:

Refractive Indices of Gypsum.

Wave-length.	Index α.			Index β.			Index γ.		
	12°.	98°.	105°.	12°.	98°.	105°.	12°.	98°.	105° C.
Li	1·5178	1·5162	1·5154	1·5201	1·5166	1·5158	1·5270	1·5247	1·5243
C	1·5184	1·5168	1·5160	1·5207	1·5172	1·5164	1·5276	1·5253	1·5249
Na	1·5207	1·5193	1·5184	1·5230	1·5196	1·5188	1·5299	1·5277	1·5274
573	1·5213	1·5199	1·5190	1·5237	1·5201	1·5194	1·5307	1·5284	1·5280
Tl	1·5231	1·5219	1·5209	1·5255	1·5222	1·5213	1·5325	1·5304	1·5300
F	1·5262	1·5248	1·5239	1·5285	1·5252	1·5243	1·5355	1·5332	1·5330
G	1·5303	1·5294	1·5285	1·5328	1·5299	1·5289	1·5400	1·5379	1·5377

The α and β indices interchange vibration-directions at about 91° C.; the vibration-direction for γ remains for all temperatures that of the first median line lying in the symmetry-plane. A comparison of the values of α and β determined at 98° C. shows that the minimum difference, 0·0002, is attained for light of wave-length 0·000573 mm., while equal differences, 0·0003, are observed in the case of sodium- and thallium-light, and still greater, but also equal differences, 0·0004, are found for lithium- and for F-light.

CHAPTER L

ROTATION OF THE PLANE OF POLARISATION BY CRYSTALS

THE phenomenon of optical activity, or rotation of the plane of polarisation of light, is not confined to the well-known liquids which display it, such as solutions of sugar and of many organic substances, but is likewise exhibited by many crystals belonging to the eleven enantiomorphous classes possessing lower degrees of symmetry (no plane of symmetry) than the full symmetry of their system, as explained in Chapter IX. (pages 131 and 132). Indeed the phenomenon itself was first observed in rock crystal, quartz, dioxide of silicon, SiO_2, so long ago as the year 1811, by Arago. Owing to the nature of the inner structure, which is often of a screw or spiral character as in the case of quartz, the two rays propagating themselves through the crystal, instead of vibrating in definite planes, are circularly polarised as in the quarter-wave mica plate. On reaching the second surface of the crystal-plate, one is retarded behind the other by reason of the difference in velocity, and possibly also because of difference in length of path, one moving more obliquely than the other. Two such circularly polarised rays, on attaining the second surface, will thus in general be in different phases. On emerging into the air each of these two circular motions, right-handed and left-handed, may be represented by a pair of forces, one radial and the other tangential. The two tangential forces are in opposite directions and destroy each other, but the radial forces are each directed towards the centre of the original circular movements, and so compound on leaving the crystal into a rectilinear vibration which is rotated from the original direction by an amount (half the difference of phase on emergence) depending on the retardation of one of the original circular motions behind the other. The amount of rotation is a minimum for rays corresponding to the red end of the spectrum, and a maximum for the violet end. Biot, who investigated the relationship between the colour of the light and the angle of rotation, found that the latter is approximately inversely proportional to the square of the wave-length.

Hence, not only is the direction of vibration of the light rotated by such crystals, but the rays are also dispersed by them; for the differently coloured rays, after emergence, will be vibrating in planes differently inclined to the original plane of polarisation of the polarising

Nicol prism, and the analysing Nicol will require to be rotated to different extents for the different colours, in order to restore the dark field. Or, if colour be produced, the complementary colour to that extinguished will be displayed at each position of the analyser. For a given thickness of quartz, for instance, cut perpendicularly to the axis, along which the property is exhibited at its maximum, the order of the colours is inverted when the direction of rotation of the analyser is reversed.

The following general formula has been shown by Boltzmann to express more accurately than Biot's approximation the relationship between ρ, the angle of rotation for a plate one millimetre thick, and λ, the wave-length in air of the light employed :

$$\rho = \frac{A}{\lambda^2} + \frac{B}{\lambda^4} + \ldots$$

The amount of rotation also depends directly on the thickness of the crystal-plate, a plate twice as thick as another affording double the angle of rotation for light of the same wave-length, and the interference colours afforded under crossed Nicols in white light become less brilliant as the thickness increases beyond that corresponding to colours of the first two or three orders of Newton, passing into white of the higher orders. It takes a much greater thickness to bring about this result, however, than in the case of interference caused by double refraction. The amount of rotation also obviously depends on the orientation of the ray within the crystal, becoming less as the orientation departs from that for the maximum effect, which in the case of quartz and other uniaxial substances is the direction of the optic axis.

The interesting fact was pointed out in Chapter XXII., and illustrated in Figs. 311 and 312 (page 355), that right- and left-handed crystals of quartz are distinguished by the appearance on the right and left respectively of the subsidiary faces of the forms s and x, dextro crystals showing $s = \{412\}$ and $x = \{41\bar{2}\}$, and lævo crystals showing the complementary $s = \{\bar{4}21\}$ and $x = \{\bar{4}2\bar{1}\}$, the symmetry of quartz being that of the enantiomorphous trapezohedral class (class 18) of the trigonal system.

Fresnel's Prism.—That the above explanation of optical rotation is correct is confirmed by the result of an interesting experiment carried

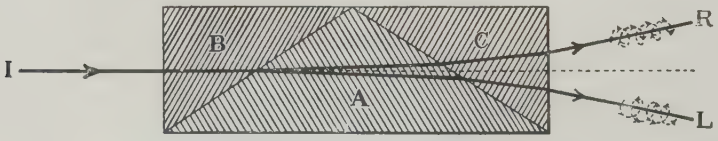


FIG. 785.—Fresnel's Compound Quartz Prism, and Isolation by its Means of two oppositely Circularly Polarised Rays.

out by Fresnel, who constructed a compound prism of the two varieties of quartz, of the kind shown in Fig. 785, by which he was actually enabled to separate the two oppositely rotating rays. It was composed of an

obtuse-angled prism of right-handed quartz A to which were cemented, one on each side, the two halves B and C of another prism of left-handed quartz, the whole forming a rectangular block. All were cut and arranged so that the rays of light traversed them along the direction of the optic axis, indicated by the dotted line. The normally incident ray I becomes divided into two oppositely circularly vibrating ones in the semi-prism B, which on reaching the first surface of the prism A are refracted in opposite ways, as the more slowly circularly vibrating ray in B becomes the faster one in A, the divergence being further accentuated on reaching the second surface of A, where a further reversal occurs. The two rays which emerge, R and L, are thus vibrating in circular orbits in opposite directions, and afford, on looking through the prism, two images of an illuminated spot or slit of light or other object employed as source of light, which show no variation in brightness on rotation of an analysing Nicol held between the prism and the eye, the test for circular polarisation. Moreover, when a quarter-wave mica plate is introduced one of the images disappears, namely, that one which was formed by light vibrating in a circular orbit opposite to that permitted by the mica, thus proving by their diverse behaviour to this test the opposite nature of the circular polarisation of the two rays.

Von Lang has also since shown that a single 60°-prism of quartz, cut so that the bisecting plane is perpendicular to the optic axis, affords in the same way, at minimum deviation, two oppositely circularly vibrating rays, about half a minute apart. The specific rotation ρ, according to Pockels, is related to the velocities of the two circularly polarised rays O_r and O_l in the following manner :

$$\rho = \frac{\pi}{\lambda}\left(\frac{1}{O_r} - \frac{1}{O_l}\right).$$

Interference Colours displayed by Plates of Optically Active Crystals, especially Quartz.—Calcite and quartz, as we have seen in Chapter XXXIX., are both uniaxial crystals, and a plate of calcite cut perpendicularly to the optic axis shows neither double refraction nor polarisation effect in parallel polarised light, remaining quite dark under crossed Nicols. On the other hand, a plate of quartz normal to the optic axis, even one seven or eight millimetres thick, shows bright colour in the dark field, truly even all over when the plate is furnished with a pair of surfaces which are truly plane and parallel. Moreover, the colour changes and passes through a great variety of tints (each being chiefly complementary to a colour of definite wave-length which is extinguished) as the Nicol analyser is rotated, and never becomes either colourless or dark. When the light is homogeneous, monochromatic, extinction is produced for a specific position of the analyser, corresponding to the amount of rotation of the plane of polarisation by a plate of that thickness for the wave-length employed. The angle of rotation from the crossed position becomes greater as the violet end of the spectrum is approached, and the direction is right or left of the zero position of the crossed Nicols (at which more or less light is transmitted) according as the plate belongs

to a right- or a left-handed crystal.[1] Plates of quartz cut obliquely to the optic axis also exhibit rotation, but the phenomena are complicated by the introduction of double refraction, and cannot be studied alone. Eventually, when the obliquity becomes considerable, the circular polarisation, already become elliptical on leaving the direction of the optic axis, passes into two ordinary plane vibrations, and thus a plate parallel to the optic axis shows no rotation, but only ordinary double refraction.

The colour exhibited in white light by such a plate of an optically active substance has already been shown to be more or less complementary to that extinguished. The colour varies, as will be clear from the preceding statement, with the position of the analyser with respect to the polariser, the variation being greatest when the colour extinguished is that of greatest intensity in the spectrum, namely, yellow in the neighbourhood of wave-length 0·000550. In the case of quartz

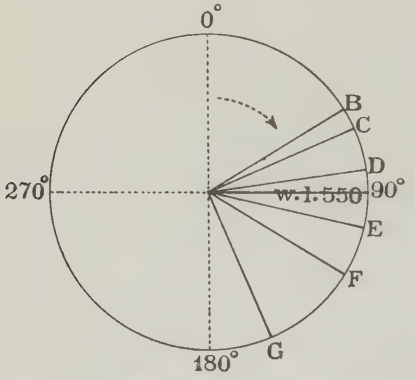


FIG. 786.—Angles of Rotation for Right-handed Quartz Plate 3·75 mm. thick.

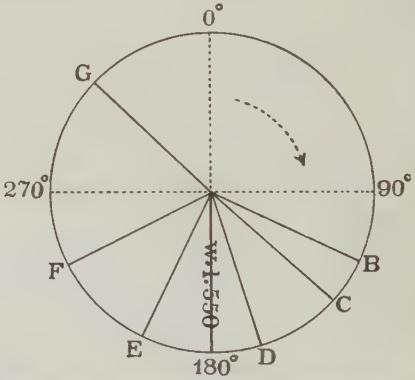


FIG. 787.—Angles of Rotation for Right-handed Quartz Plate 7·5 mm. thick.

under crossed Nicols this occurs for a plate perpendicular to the axis of 7·5 mm. thickness, and with parallel Nicols for one 3·75 mm. thick. For a plate of 7·5 mm. rotates this yellow ray for 180°, while one of 3·75 mm. thickness rotates it for 90°. This is graphically illustrated in the two diagrams Figs. 786 and 787, which give with strong lines

[1] Considerable confusion has been introduced into the subject of optical rotation by the fact that chemists, in their use of the polarimeter for the determination of the rotation of the plane of polarisation by optically active substances (chiefly liquids or solids in solution, but occasionally the solids themselves), have adopted a different convention, as regards the sign of the rotation, to that employed by physicists and crystallographers, who refer to the actual occurrence in the crystal itself. For instance, the right-handed quartz of the crystallographer actually rotates the plane of polarisation of light in the opposite direction to the so-called dextro-camphor of the chemist. The latter regards a rotation as right-handed or dextro when it appears clockwise to the observer looking through the eyepiece of the polarimeter. But the crystallographer regards himself as travelling with the beam of light, that is, as looking along the direction of propagation of the light; if the movement of the light in the crystal is like that of a right-handed screw, clockwise, the crystal is right-handed or dextro-gyratory, and if the light moves in left-handed screw fashion, anti-clockwise, the crystal is lævo-rotatory or left-handed. It is very important that this should be quite clear.

the rotation of rays of wave-lengths corresponding to those of the Fraunhofer lines B, C, D, E, F, and G, and to wave-length 0·000550, by right-handed plates of these two thicknesses. The interference colour actually observed when wave-length 0·000550 is extinguished is the transition violet between the first and second orders of spectra in the cases of both these plates. That is, a plate of quartz 3·75 mm. thick gives the transition tint when the Nicols are parallel, while one of 7·5 mm. thickness gives it when the Nicols are crossed, a rotation of 180° having the same effect as no rotation at all, as it merely brings about the crossing again. A slight rotation of the analyser from the position for the violet transition tint, to the right (clockwise) or left (anti-clockwise), according as the crystal is right-handed or left-handed, causes the colour to change to red (first order). On the other hand, a rotation of the analyser contrary to the rotatory character of the plate causes the violet transition tint to change to blue or green (second order).

The colours afforded by plates thicker than 7·5 mm. are less brilliant; for when the angle of rotation for red becomes a multiple of 180°, other colours than that may also be rotated for still higher multiples of 180°, and be simultaneously extinguished by the analyser. A plate 10 mm. thick rotates the bright red near C for 180° and a plate of 20 mm. for 360°, two semicircles. A 20-mm. plate, however, also rotates the yellowish green for three semicircles, and the indigo blue for four semicircles, so all three colours are extinguished under crossed Nicols, and white of the higher orders is largely admixed with the colour shown. More colours still are simultaneously extinguished with yet greater thicknesses of plate, and eventually pure white light is afforded. On the other hand, the colour becomes again enfeebled when the thickness is much less than 3·75 mm. A plate 1 mm. thick gives only feeble tints, one of 0·5 mm. feebler still, and one of only 0·1 mm. only gives rotations for red and violet of 1·7 and 4·4 degrees, and under crossed Nicols shows practically no light.

The Biquartz.—A most valuable application of the facts stated in the preceding section is found in the biquartz, a double plate of 3·75 or 7·5 mm. thickness, composed of one semicircular plate of right-handed quartz and another of left-handed quartz, both cut truly perpendicular to the axis; the two normally ground and polished plane bases of the semicircles are cemented together with balsam so as to show only a faint line when the plate is regarded normally, as shown in Fig. 788, the different-handed nature of the rotation of the two halves being indicated in the figure by the shading. Such a composite plate gives the transition violet equally throughout when the Nicols are parallel (for a 3·75-mm. plate) or crossed (for a 7·5-mm. plate), and a slight rotation of the analyser causes one side to become red of the first order and the other blue or green

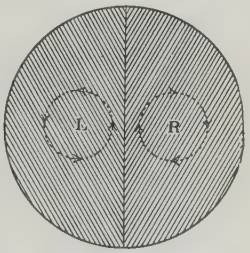


FIG. 788.—The Biquartz.

of the second order spectrum. In sodium light such a biquartz appears equally brightly yellow in the two halves, when the analyser is parallel or crossed in the two cases, while a very slight rotation of the analyser is sufficient to effect a clearly perceptible difference of intensity between the two halves, as indicated in Fig. 789.

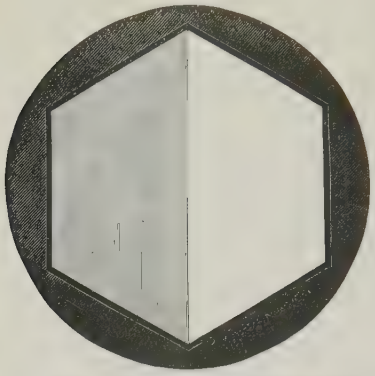


FIG. 789.—Appearance of a Biquartz with Analyser slightly rotated.

A biquartz thus affords a means of rendering more exact the adjustment of the analysing Nicol to the crossing position with the polariser, and also for detecting rotation of the plane of polarisation by any other plate or a cell of liquid introduced between it and the polariser, after the latter and the analyser have been set for the transition tint. For obviously any disturbance of the plane of polarisation will affect the two sides of the biquartz oppositely. The biquartz is consequently much used in polarimeters or saccharimeters, polariscopes for the determination of the optical rotation of liquids and solutions (see Chapter LV.), and may be effectively used also for the practical determination of the angle of rotation of an optically active crystal-plate.

Sometimes it is possible to obtain a natural biquartz, cut from a natural twin crystal of right- and left-handed rotatory power and crystallographic development. The author possesses two such natural biquartzes of 3·75 mm. thickness, in which the violet colour produced in both halves when the Nicols are parallel is exquisitely even and beautifully delicate, while the line of junction of the two individual crystals is invisible, except for a very thin white line in one case, and a mere trace of such in the other, the plane of composition of the twin being perpendicular to the plate. On the slightest rotation of the analyser the two halves pass respectively into brilliant red and blue. With crossed Nicols an even yellow is shown, with a thin black line of demarcation between the two semicircles; the yellow passes rapidly on rotation of the analyser into orange on one side and green on the other.

When the plane of the plate is not at right angles to the plane of composition of the twin, but inclined, the effect with parallel Nicols is to produce a broad white band extending for the width of the inclined overlapping of the two halves, and under crossed Nicols a black band, as shown in Fig. 789*a*, the dark field being produced along this strip where the two opposite rotations neutralise each other. It is similar to the dark band produced in the centre of the field by a rectangular block composed of two superposed wedges of oppositely active quartz, Fig. 807, as described on page 1104. Indeed when the plate is sufficiently thick (7·5 mm. serves admirably) not only is the black central band seen, but also two spectrum bands are observed, one on each side of it, separated from it

by a white space. The effect can be readily and exactly imitated, by constructing a thick double-plate of quartz, composed of two halves of respectively right-handed and left-handed quartz, each of 7·5 mm. thickness, and each of which has had the edge-face of junction ground and polished at about 30° or so from perpendicularity to the plate, the two parts being cemented by hard balsam dissolved in turpentine in the usual manner for a biquartz. Fig. 790 of Plate VIII. shows the effect with such an artificial composite plate of large size possessed by the author, when placed in parallel light between the crossed Nicols of the projection polariscope. It forms a very beautiful object as seen projected on the screen, the two halves on the two sides of the central junction-strip polarising brilliantly in even complementary colours.

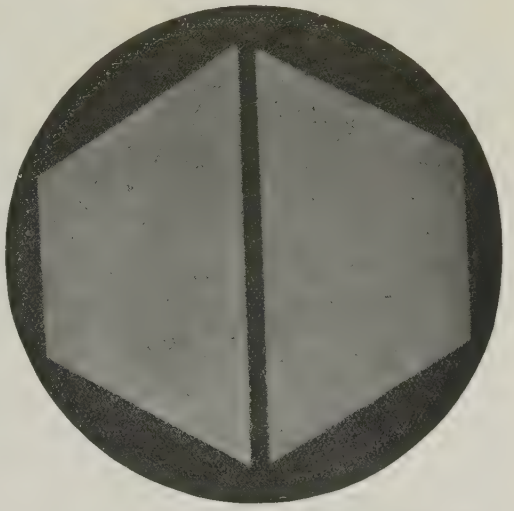


FIG. 789*a*.—A Natural Biquartz between Crossed Nicols, Plane of Junction somewhat Oblique to Plate.

The effect of a black band with flanking spectra is very similar to that obtained, due to double refraction and not to optical activity, when two thin wedges of quartz are cemented together to form a parallel plate, one wedge being cut so that the optic axis is parallel to the edge of the wedge, and the other with the optic axis perpendicular to the edge. When such a composite quartz plate, known from its first constructor as a "Babinet Plate," is placed on the polariscope stage, and rotated to the 45° position with respect to the planes of vibration of the crossed Nicols, there is observed on the screen a deep black band in the centre, parallel to the edge of the wedge, and a number of spectrum bands on each side, separated by white equal interspaces, the rainbow-coloured bands showing the orders of Newton's spectra. The effect is illustrated as far as is possible in black and white in Fig. 838 in Chapter LII., which is a direct reproduction of a photograph of the screen-picture.

While occasionally the Brazilian twinning of quartz, parallel to a pair of faces of the second order hexagonal prism $\{10\bar{1}\}$ or $\{11\bar{2}0\}$ as described on page 507 and illustrated in Fig. 410, furnishes a section-plate which is a perfect natural biquartz, with the edge-plane of junction so truly perpendicular to the plate as to afford a dividing line only visible when the analysing Nicol is rotated from its position of exact crossing to the polarising Nicol; and while it still oftener affords a section-plate with an oblique edge-plane of junction, giving the effects seen in Figs. 789*a*

and 790 ; it much more frequently occurs in an irregular and even erratic manner, giving rise to the most remarkable and varied effects in parallel polarised light when a section-plate is cut perpendicular to the axis, the surfaces of contact taking every variety of shape and inclination. Such a striking case is reproduced in black and white from the projected screen-picture in Fig. 791 on Plate VIII. Fig. 792 of Plate VIII. is the reproduction of a screen-picture afforded by a particularly interesting section-plate, in which there are repeated 60°- or 120°-wedge-shaped intrusions of one variety of quartz into a greater mass of the other variety, the border of the wedge being composed of a ribbon, the outer edges of which are spectrum-coloured, and the central line of which is formed by the deep black band, separated on each side from the spectrum by a white strip. When the photograph was taken the upper homogeneous part was coloured a brilliant green, and the lower part, appearing black in the photograph, was a deep red.

Another very instructive mode of occurrence of the twinning is that which takes a parallel rectilinear strip-like form, due to repeated and more or less regular alternation of the right- and left-handed varieties of quartz. An excellent example is shown in Fig. 793 of Plate VIII., which represents the effect, as seen in parallel light with crossed Nicols, with a plate of quartz 7·5 mm. thick, one half of which is composed of left-handed quartz, giving a rich rose-red colour on the screen (or on using the projection polariscope as a table instrument), while the other half consists of an alternation of parallel straight strips of right- and left-handed quartz, joined obliquely to the plate surface, the black band, white bands on either side, and flanking spectra being repeated several times before the edge of the plate is reached. This plate, indeed, exhibits on the grosser scale what occurs in amethyst in a more minutely laminated and accurately regular manner, as illustrated, facing page 510 in Figs. 414 and 415, on Plate III. The alternate strips in amethyst are reduced to mere lines, the sections of laminæ or films of almost microscopic tenuity, their number being correspondingly enormously increased.

Determination of the Rotatory Power of Optically Active Crystals.—The direct determination of the angle of rotation of the plane of polarisation by a crystal-plate is conveniently carried out with the aid of a special fitting to the polariscope of the von Groth universal apparatus already referred to in Chapter XLVIII., and illustrated in Fig. 762 (page 1045), in connection with its use in optic-axial-angle determinations. The apparatus as arranged for the ordinary determination of optical rotation, with the aid of the monochromatic illuminator of Chapter XLIV., is that already illustrated in Fig. 763 on page 1046, except that the polariscope is specially fitted for use as a polarimeter (instrument for measuring the rotation of the plane of polarisation of light), in a manner which is shown in Fig. 794. This Fig. 794 also shows the illuminator in use as a spectroscope, for the analysis of the coloured light transmitted by the biquartz, and localisation of the extinguished wave-length, a particularly accurate method of determining the optical rotation which will be fully described in a later section of this chapter (page 1096).

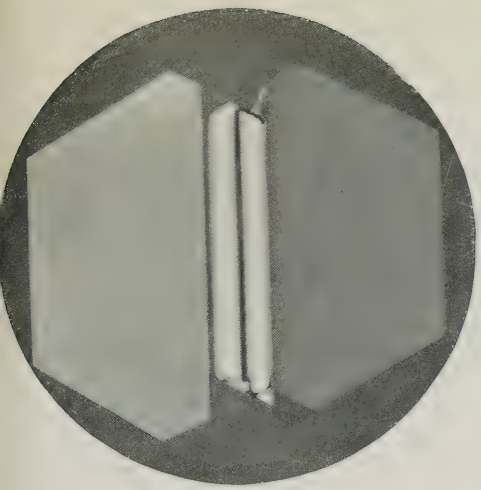


FIG. 790.—Artificial Biquartz 7·5 mm. thick, the two Halves obliquely joined to afford the Black Band and flanking Spectra.

FIG. 791.—Irregular Brazilian Twinning of Right- and Left-handed Quartz, shown by Plate perpendicular to the Axis.

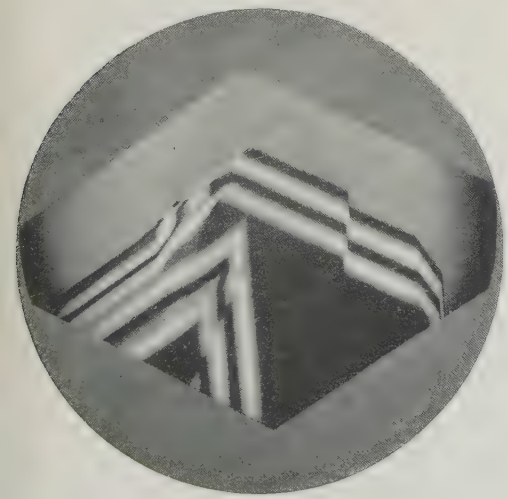


FIG. 792.—Intrusive 60° and 120° natural Twinning of Right- and Left-handed Quartz, showing Ribbons with central Black Band where oblique Overlapping occurs.

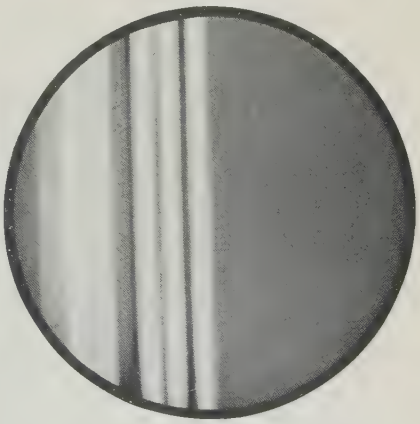


FIG. 793.—Naturally Twinned Quartz Plate 7·5 mm. thick, the Right Half being of Right-handed Quartz, and the Left Half of alternating Right- and Left-handed Quartz obliquely joined.

PHOTOGRAPHIC REPRODUCTIONS OF SCREEN PICTURES

Afforded in Parallel Polarised Light by Quartz Plates composed of Right- and Left-handed Varieties.

Plate to face page 1086.

The system of converging lenses *a*, *b*, *c*, *d* (Fig. 762) is removed from the polarising tube *i*, so as to leave it arranged as for parallel light instead of for convergent light. Further, the whole analysing tube *t* is removed (it is shown standing up on the spectroscope base-board in Fig. 794), and replaced by a special rotatable cap ϵ, fitting over the circle plate *m* which carries an engraved silver vernier, and which has been permanently attached to the circular widening *g* of the front column *b* (*f* in Fig. 762) for the express purpose of this measurement. The cap is provided with a bevelled silver divided circle, for use with the vernier engraved on *m*. The front of the cap carries a short tube θ for the reception of the Nicol analyser *x*, and the whole cap is then rotated until the dark field is produced with the large polarising Nicol in the polarising tube *i*. It is sometimes an advantage to place in front of the analysing Nicol the small-aperture cap with its little lens, shown at κ leaning up against the tube *t* in Fig. 794. The crystal-plate is suspended from the crystal-holder δ, or is held in a special pincette of platinum foil held in turn by the ordinary one δ, and it requires to be first adjusted, perpendicular to the optical axis of the polarising and analysing tubes, with the aid of the adjusting and centring movements γ and β.

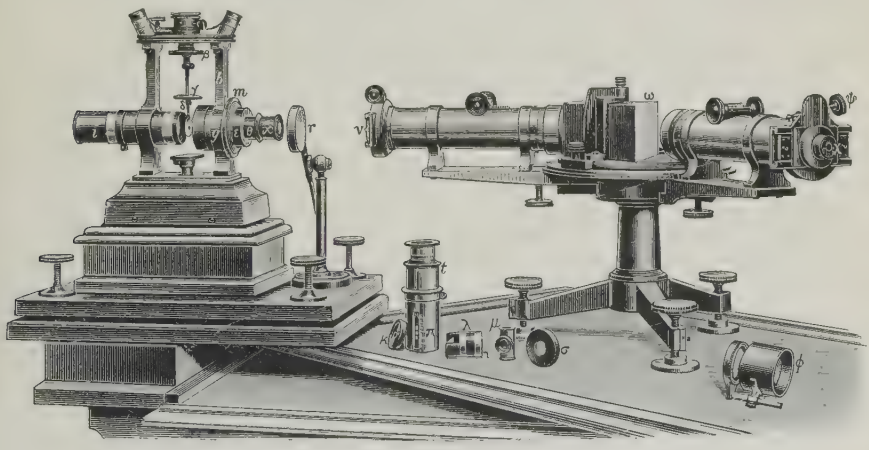


FIG. 794.—Determination of Angle of Rotation of Plane of Polarisation by an Optically Active Crystal.

This adjustment has to be effected absolutely, as otherwise the rays will traverse a greater thickness of the crystal than is represented by its measured thickness. To enable it to be accurately achieved, the cap and the analysing Nicol are temporarily withdrawn, and replaced by the ordinary analysing tube *t*; but instead of the analysing Nicol, which is left attached to the removed cap, there is inserted a so-called Gauss's mirror, a short open tube carrying a plate of truly plane-parallel glass, rotatable on an axis diametral to the tube, the rotation being effected by a little bent lever the handle of which projects outside in front. It is shown at λ in front of the apparatus, and separated from *t* for the sake of clearness, in Fig. 794. Or the Becker fitting described on page 41 and also shown in Fig. 24, and in front at μ in Fig. 794, may be adapted instead. The rays from a goniometer or table lamp placed to one side of the instrument are admitted through a slot (*s* in Fig. 762) in the tube *t*, and are reflected from the glass-plate mirror normally to the crystal, and thence back again, passing straight through the glass plate to the observer's eye. In order to serve as a signal, the glass plate bearing an engraved micrometer scale and also a vertical diametral line at right angles to the horizontal one of the scale, which is given by Fuess with the universal apparatus for use in approximate estimations of optic axial angles, should

be placed in position at π in the tube t, if not already there; the reflected image of the cross-lines and scale is then made, by adjustment of the crystal-plate (reflecting the image) exactly normal to the axis of the tube t, to coincide with the actual cross-lines and scale themselves, as seen directly.

After this important adjustment has been carried out, the tube t is removed and the cap and Nicol reinstated. The determination of rotation can then be carried out either (1) without or (2) with the aid of a biquartz. The former simpler case will first be considered.

(1) The Nicols being accurately crossed for production of maximum darkness, the crystal-plate will appear coloured in white light, and bright in monochromatic light with the colour corresponding to the wave-length employed. Using either sodium light or its equivalent furnished by the monochromatic illuminator as one of the wave-lengths for which a determination is to be made, in the manner shown in Fig. 763 (p. 1046), it will be found to be necessary to rotate the analysing Nicol, together with the large divided circle-cap which records the amount of the rotation much more finely than the circle of the Nicol itself, for some degrees on either one side or the other in order to restore the dark field. By approaching this position from the original crossed position and taking a reading, and then going too far and returning to the position of extinction and taking a second reading, and afterwards taking the mean of the two readings, or better still the mean of several such pairs of readings, a close approximation to the extinction position will be obtained. The angle of rotation required is the difference between this mean reading for extinction and the reading for the crossed position of the Nicols.

(2) The determination of the extinction position can be more delicately achieved with the aid of a biquartz of either 7·5 or 3·75 millimetres thickness. The biquartz is inserted in another cap, which acts also as a mount and fits over the further end of the tube projecting through the collar g, nearest the crystal. Its fine diametral line of cementation if it be an artifical biquartz (such a biquartz is shown in front at σ), or line of composition if a natural twin (a natural biquartz being in position in the cap), is arranged vertically (except when a spectroscope is to be used to analyse the colours, when it is arranged horizontally, as will be described later, on page 1096), and this line serves excellently for focussing purposes when the small-lens cap supplied with the apparatus is used in front of the Nicol in order to restrict the eye-opening and enlarge the field. The junction-line may also be utilised as the line of reference instead of the micrometer scale and cross-lines if desired or convenient. The crystal-plate should be raised out of the field while the biquartz is adjusted to afford absolutely identical transition tints in the two halves, the Nicols being parallel if the biquartz be of 3·75 mm. thickness, or crossed if it be a 7·5-mm. plate. Then on lowering the crystal into position again, after confirming that the normal adjustment of the plate has not been impaired, by using the Gauss or Becker fitting and the dividing line of the two halves of the biquartz itself as reference line, these two halves will be observed to have taken up different tints, due to the rotation of the plane of polarisation by the crystal.

The analysing Nicol is then rotated through the angle of this rotation, to the position at which the transition tint is equally restored in the two halves of the biquartz. The transition violet should be approached from the two different sides several times, equal in number, and the mean of the readings taken as the true position; the difference of this from the reading for the original transition tint when no crystal was in the field is the angle ρ of rotation required.

This value, however, will only be the mean value of the rotation for the middle of the spectrum, and if the dispersion of the rotation be considerable for different wave-lengths, it can only be regarded as an approximate value. Hence, in truly accurate work monochromatic light is essential, and the observations should at least be made for sodium light, equality of intensity of illumination of the two halves of the biquartz being accepted as indicative of the true position of the rotated plane of polarisation.

To render the observations complete, however, they should be made for a series of wave-lengths, and when the spectroscopic monochromatic illuminator described in Chapter XLIV. is available (arranged as in Fig. 763) the same six wave-lengths as have been recommended in all the other optical work may conveniently be employed, namely, those corresponding to Li-light, C-light, Na-light, Tl-light, F-light, and violet hydrogen light near G of the spectrum.

There are many other devices which may be employed instead of a biquartz to enhance the sensibility of the determination of the rotation angle. A Laurent half-shadow plate may be used, as in the polarimeter or saccharimeter (a polarimeter used chiefly for observing the optical rotation of sugar solutions, and thereby determining their strength) of that name, in which case monochromatic light is essential, sodium light giving very sharp results. The Laurent plate is a plate of glass of which one half is covered with a half-wave mica, selenite (gypsum), or quartz plate, so that the circular field of the polariscope is divided by the diametral line of junction, as in the case of the biquartz. The two halves appear equally bright when the analyser is arranged parallel to the plane of polarisation of the light reaching it, but the least divergence from parallelism introduces a considerable difference of intensity. In the event of the Laurent plate having one-half constructed of quartz, the latter is cut parallel to the axis, and of such thickness that there is a retardation between the ordinary and extraordinary rays of exactly one half-wave.

Another device for enhancing the sensitiveness of the determination is to replace the Nicol analyser by a Jellett compound calcite prism. This little-known but very valuable prism was described by Jellett to the British Association at their meeting in the year 1860.[1] It enables the plane of polarisation of light to be determined with great precision. It consists of a long prism of calcspar, which is first reduced to the form of a rectangularly terminated prism by grinding off its ends, and is then sliced lengthwise by a plane nearly but not quite perpendicular to the principal plane containing the shorter diagonal of the rhomb and the optic axis. The two parts are joined in reversed positions, and a diaphragm with a circular opening is placed at each end. The light which passes through both diaphragms produces a circular field divided by a diametral line into two parts, in which the planes of polarisation are slightly inclined to one another. The Calderon stauroscopic plate, described on page 976, differs in regard to the direction of cutting, the plane of cementation of the two halves being nearly parallel, instead of perpendicular, to the principal plane just referred to. When light which has been previously plane polarised is transmitted, it will be extinguished in the two parts of the field for positions which are fairly close together, and the light will become of uniform intensity in a position midway between the two. When, therefore, the double prism is arranged to give this equality of tint on placing it in the path of the light rays leaving the polarising Nicol, and the optically active crystal-plate is then introduced, the balance of intensity in the two halves will be

[1] *British Assoc. Reports*, 1860, vol. 2, 13.

upset; the Jellett double prism is then rotated to follow the rotation of the plate, and arrested when the two halves are again equally illuminated. The difference of the circle readings corresponding to these two positions will then obviously afford the required angle of rotation ρ.

Although each of these forms of sensitiveness-enhancer has its special merits, as above recorded, the use of a perfectly constructed biquartz is, however, on the whole perhaps the most satisfactory of all bisected field, half-shadow devices for enhancing the sensitiveness of this important determination of optical rotation, and any slight error of setting of the biquartz and the crystal-plate to exact normality to the polariscopic axis may be corrected by taking a second set of readings with the analyser rotated 180° from the position which it occupied in the first series.

In many polarimeters or saccharimeters now, however, the sensitiveness-enhancing device is a triple one composed of three vertical strips; the central strip shows one intensity for a slight deviation from the rotation position, and the two flanking strips on each side, being similarly orientated, exhibit the other intensity to an equal degree, that is, exhibit equally another different intensity. It appears easier to discriminate the difference of intensity when the observer has a central strip of one intensity and two equally different ones on each side to deal with, the required position when all three are equally intense being very sharply determinable. Two of the best of these three-strip-field devices will be described in the next section, concerning the optical activity of solutions.

Polarimeters for Rotation of Liquids.—It is often desirable to investigate whether an optically active crystallised substance also exhibits optical activity when the crystals are dissolved in a solvent, in order to discover whether the activity is due to the enantiomorphism of the chemical molecules or of the point-system on which the crystal structure is built up, or to both causes. If the solution as well as the crystals rotate the plane of polarisation of light, the molecules as well as the crystal structure are enantiomorphous. But if the solution be not optically active, while the crystals are, then the enantiomorphism is due simply to the structure of the point-system. Many pure liquid substances themselves, especially carbon compounds, also rotate the plane of polarisation of light, although usually to a much smaller extent than solid crystals. An interesting fact about the molecules of quartz, the prototype of optically active crystals, has been revealed, namely, that fused quartz, now such a common material as used for unbreakable laboratory vessels, does not rotate the plane of polarisation of light, the optical activity of quartz thus obviously being due to its two complementary types of screw structure alone, and not to the molecules of SiO_2.

Polarimeters, the instruments for the measurement of the optical rotations of liquids or of solutions in liquid solvents, are often termed saccharimeters, as they have come into extensive use for the purpose of determining the strength of aqueous solutions of cane sugar, $C_{12}H_{22}O_{11}$, in sugar works and refineries. For the general law was discovered by Biot,

that the amount of rotation of the plane of polarisation of light is directly proportional to the percentage weight of the optically active crystalline substance (in this case cane sugar) contained in the solution, and to the length of the column of the liquid solution through which the light passes. Thus a 20 per cent. solution affords a rotation twice as great as a 10 per cent. solution, and a tube 30 centimetres long filled with the solution will give three times the amount of rotation that a tube of 10 centimetres full of liquid will exhibit. This fact as regards length of column is analogous to that referred to on page 1080, that the amount of rotation in the case of a crystal is directly proportional to the thickness of the crystal plate employed. In the case of solutions, however, care requires to be taken not to employ them too dilute, for then electrolytic ionic dissociation is liable to occur with disturbing effect. Complicated formulæ have been given by various observers from time to time, beginning with Biot in 1838, to express the minute effect of the solvent on the optical rotation of the substance dissolved; for the solvent supposed to be without action, being non-rotating, does not altogether behave as expected, some kind of intermolecular action between the two substances being traceable. None of these formulæ, however, have proved fully satisfactory, probably because any such minute action as occurs is specific to the particular solvent and dissolved substance in question. In any case such effects are almost within experimental error, and are practically negligible.

The kind of relationship between solid crystals and liquids (either pure substances or solutions), as regards amount of optical rotation, will be exhibited by the following table. For comparison it should be remembered that it has been shown in previous pages that a plate of quartz one millimetre thick affords for sodium D-light a rotation of 21·7°, and of 17·3° for red C-light. The rotations given in this table are for red light and a thickness of liquid of one decimetre between the two end plates closing the glass-containing tube. The sign + indicates a dextro rotation, and − a lævo rotation.

Table of Optical Rotations of some Liquids.

Essence of turpentine	−29·6°
Pure dextropinene from American spirit of turpentine, b.p. 156°	+21·5
Lævopinene from French turpentine oil, b.p. 156·5°	−40·3
Essence of carraway	+65·8
Essence of Seville oranges	+78·9
50 per cent. aqueous solution of cane sugar	+33·6
6 per cent. alcoholic solution of quinine	−30·0

Oil of turpentine, which has been known for a very long time to rotate the plane of polarisation of light, is usually a mixture of a considerable number of isomeric turpenes known as pinenes and camphenes, all of the formula $C_{10}H_{16}$; and both the amount and the sign of its rotation must obviously depend on the composition, that is, on which of the isomerides are present and their relative amounts, as each has its own specific rotation. Two varieties, however—American spirit of turpentine and French oil of turpentine—are almost pure dextropinene and lævopinene respectively,

and the rotations of these are given in the table. It is interesting that Biot in 1819 came to the conclusion that organic liquid substances which are optically active exhibit the property also in the gaseous state, and Gernez in 1864 proved this to be the case for the vapour of turpentine. This is clearly another proof of the enantiomorphism of the chemical molecules.

Every optically active substance has now been shown to possess its own **specific coefficient of rotation.** For solids the amount of rotation of a plate one millimetre thick and for sodium yellow light is taken as the specific coefficient, and it is denoted by ρ as already described. For liquids the specific coefficient is expressed as $[\alpha]_D^{20°}$.

The value of the rotation angle, here denoted by α, is assumed in this coefficient to be determined at the temperature of 20° C., and for sodium D-light. If l be the length of the column of liquid used, as measured between the two parallel end-plates of the tube and expressed in decimetres, and c be the number of grammes of the substance in one cubic centimetre of the liquid (whether it be a solution or a pure substance), then :

$$[\alpha]_D^{20°} = \frac{\alpha}{lc}.$$

Instead of c we may write d, and take it to mean the density of the liquid, for this is obviously the same as the weight of 1 c.c., the specific gravity being the weight of 1 c.c. of the substance compared with that of an equal bulk of water at 4° C. The specific rotation $[\alpha]_D^{20°}$ is thus the angle through which the plane of polarisation of sodium D-light is rotated by passing through a column of the liquid substance one decimetre long and containing one gramme of the substance in one cubic centimetre. If the liquid be a solution of a solid substance in an optically inactive solvent the expression for $[\alpha]_D^{20°}$ requires another factor, representing the concentration ; l as before is the length of the column of solution in decimetres, d is the specific gravity of the solution, and p represents grammes of the optically active substance in 100 grammes of solution. Or instead of p we can write its equivalent two quantities actually determined, namely, n the grammes of solution containing g grammes of substance. We then have :

$$[\alpha]_D^{20°} = \frac{100\alpha}{l \,.\, d \,.\, p} \text{ or } = \frac{n \,.\, \alpha}{l \,.\, d \,.\, g}.$$

For cane sugar, $C_{12}H_{22}O_{11}$, in solutions of moderate strength, up to 30 per cent., the specific rotation $[\alpha]_D^{20°}$ is 66·7° (average of determinations in most trustworthy researches).

The connection between optical activity and the presence of assymmetric carbon atoms in the molecules of organic substances, and the whole question of enantiomorphism, will be dealt with fully in Chapter LV. It will be sufficient to state here that, in the case of carbon compounds, only those compounds are optically active which possess one or more asymmetric carbon atoms, that is, atoms of carbon the four valencies of which

are satisfied by four different atoms or radical groups. Asymmetry of one or more carbon atoms is not, however, the condition for optical rotation; for many carbon compounds have such atoms of carbon, and yet are inactive, the reason most frequently being, in cases where there are two such atoms or any even number of them, the internal compensation by mutual neutralisation or symmetrisation, that is, enhancement of the internal symmetry of the molecule by the mirror-image arrangement of similar asymmetric groups within the molecule itself.

The **molecular rotation,** $[M]_D^{20°}$, a constant of some theoretical importance as regards constitutional organic chemistry, is the product of the specific

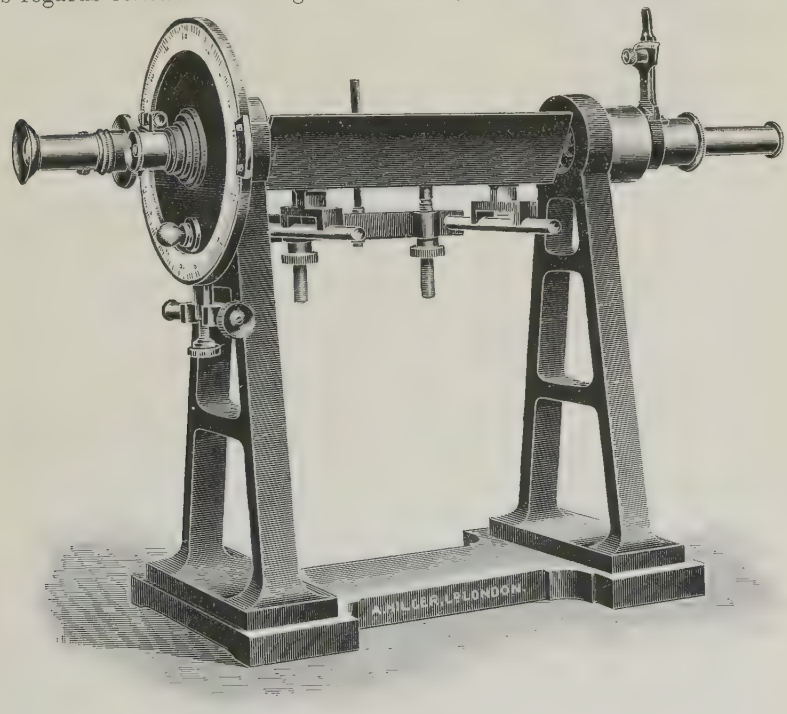


FIG. 795.—Polarimeter by Hilger.

rotation and the molecular weight, divided by 100 so as not to obtain unwieldy numbers. The value of $[M]_D^{20°}$ for cane sugar is 228·1°.

Two of the most accurate and recent forms of **Polarimeter,** for measuring the rotation of the plane of polarisation of light in liquid substances and solutions, are those constructed by A. Hilger in London, and by Schmidt & Haensch in Berlin. Fig. 795 shows the former, Fig. 796 indicates the nature of the field of view through it, showing the triple form of its sensitiveness-enhancer, and Fig. 797 represents the Berlin instrument with its accessories.

The Hilger instrument, Fig. 795, takes tubes for liquids two decimetres long, and

this length can be doubled if specially requested. Screw adjustments are provided for the accurate levelling and centring of the tube, so as to bring its axis to coincide exactly with the axis of the instrument. The polarising system is of the type devised by Lippich, and modified by Landolt so as to render the half-shadow device for accurate orientation of the position of the angle of rotation one of the three-strip form, the circular field being divided, as shown in Fig. 796, into three vertical parallel strips. The illumination of the middle strip decreases in intensity when that of the two outer strips increases, and *vice versa*.

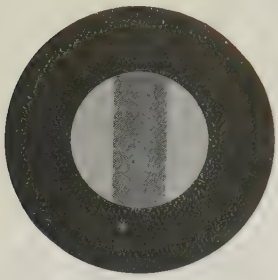


FIG. 796.—Triple Half-shadow Field of Polarimeter.

The device of Lippich consisted in placing immediately after the polarising Nicol, and just before the tube of liquid, a smaller Nicol, half covering the field, and with its vibration direction set at a small angle with that of the polariser. On illuminating with monochromatic light the field appears uniformly lighted when the vibration direction of the analysing Nicol in front of the liquid tube is perpendicular to the bisectrix of the small angle between the vibration directions of the polariser and the smaller Nicol. Landolt added a second small Nicol next the polariser, the two small prisms being in the same vertical plane arranged right and left alongside each other, but with sufficient space between them to leave a central vertical strip of the field of the polariser uncovered by either of them, thus producing the kind of field shown in Fig. 796. The reason for the greater sensitiveness of this triple-strip field, according to R. S. Clay, who has made a special study of the subject, would appear to be as follows: With the ordinary half-shadow (two-strip) field the part of the retina of the eye on which the image of the bright half of the field falls becomes fatigued, and if the two halves could be suddenly made equally bright that half which was originally brighter would appear darker than the other in consequence. But when the field is divided into three strips, of which the two outer are equal and either both darker or both brighter than the central strip, by fixing attention alternately on the one or the other dividing line the fatigue effort actually helps to increase the sensitiveness; for the part of the retina which was fatigued by the brighter strip when one dividing line was observed, is the part on which the duller light falls when the eye is directed to the other dividing line.

A mercury vapour lamp, such as that devised by Dr. Sand, or the Cooper-Hewitt lamp, described on pages 971 and 973, and illustrated in Figs. 722 and 722*b*, is found to be the best illuminant, instead of a sodium flame, as it affords greater accuracy and is more convenient. The divided circle is 7 inches in diameter, and the division is on platinoid, which does not tarnish. The double verniers read to 0·01 degree. The analyser is provided with a slow motion fine adjustment. A Ventzke scale is also provided, which affords direct readings in percentages of sugar, for use when the instrument is employed as saccharimeter in sugar estimations.

The Schmidt & Haensch polarimeter, Fig. 797, is also of the Landolt type, having the triple-field sensitiveness-enhancer. In some of the instruments supplied by the firm, especially for sugar analysis, a Jellett calcite prism (see page 1089) is employed to provide the sensitive device, and the accuracy is so high with this form of instrument that the possible error is only 0·02 of a grain in a cubic inch of sugar solution. The Schmidt & Haensch polarimeters have also been much used in organic chemical laboratories, for the determination of the optical rotation of new active carbon compounds.

There is still one other form of polarimeter which merits some description, as it involves a new principle, namely, that of Soleil. It is an

ordinary Nicol prism polariscope, arranged as polarimeter for liquids as shown in Fig. 798, by providing space for the elongated tube containing the fluid, and with a biquartz of 7·5 mm. thickness, placed between the polarising Nicol and the liquid tube, as sensitiveness-enhancer, but to which also certain special accessories are added.

The first is a plate of right-handed quartz cut perpendicularly to the optic axis and of a thickness t, placed immediately after the tube of liquid. Next to this and between it and the analysing Nicol come a pair of similar and mutually inverted wedges of left-handed quartz, such that together they form a parallel-sided plate the thickness of which can be varied from almost nothing up to $2t$, by one of the

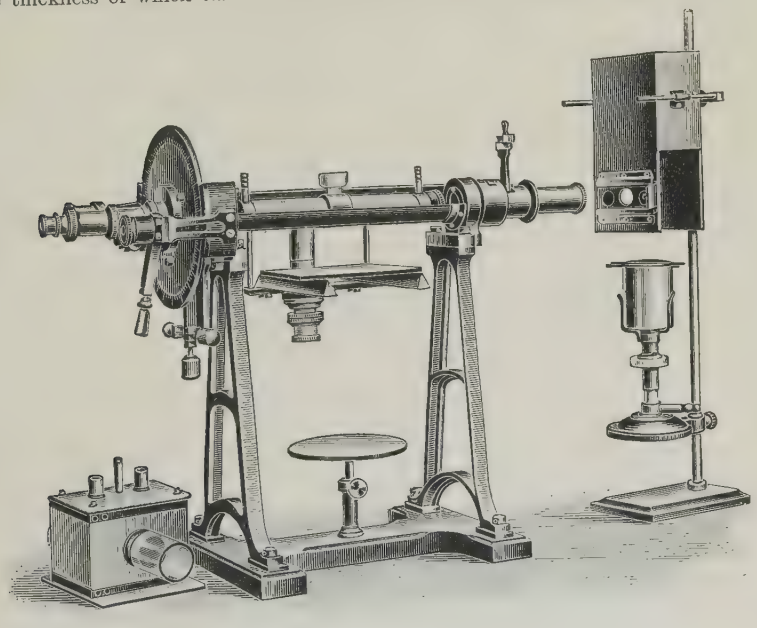


FIG. 797.—Polarimeter by Schmidt & Haensch.

wedges being made to slide by rack and pinion movement over the other, very much like the arrangement in a Babinet compensator. The bases of the two wedges, the two parallel faces of the double-wedge plate, are also perpendicular to the optic axis of the quartz, like the faces of the other, right-handed, plate. A scale is provided with one of the wedges and a vernier with the other, and they are so arranged that when the indication is zero (this being in the middle of the scale, which reads right and left of this zero) the thickness of the left-handed double-wedge plate is equal to that of the solid right-handed one ; the rotation of the latter is then exactly neutralised and compensated. The apparatus under these conditions is a simple polarimeter with biquartz, the dividing line of the two halves of the latter being focussed by the eye-piece, which takes the form of a small Galilean telescope (a combination of a doubly convex objective and a doubly concave eye-glass) in front of the analyser. The tint of passage afforded by the biquartz when the Nicols are crossed is at once upset by the slightest movement of the milled head controlling the movement of the movable wedge, the combination of quartz plate and double-wedge plate then

corresponding to the introduction of an excess of either right or left quartz, according to the direction in which the milled head is turned. Hence, if the transition tint of the biquartz has been destroyed by the introduction of the tube of optically active liquid, it can be restored by introducing an equivalent amount of right- or left-handed quartz, according to the sign of rotation of the liquid, by careful rotation of the milled head controlling the wedge. The scale reading of the compensator enables this amount of quartz thickness to be read off, and thus the rotation angle of the liquid to be determined; for it is equal to that afforded by a plate of quartz of the thickness given by the scale reading. Soleil also added an extra element to counteract the effect of colour in the liquid (many of the sugar liquids being deeply coloured) or in the light employed, if pure white light be not available. It consists of another Nicol and quartz plate, added outside the apparatus as described, either before the light enters the polariser or after it leaves the eyepiece. It is arranged to compensate for the undesirable colour by producing a complementary tint with the polariser or analyser, and it is found in practice to do this so effectually that a satisfactory transition violet is afforded by the biquartz, the determination being then as readily possible as with ordinary unstained white light.

Fig. 798 will enable the whole arrangement of Soleil's polarimeter to be readily followed. The apparatus is rendered the more suitable for saccharimetry, inasmuch

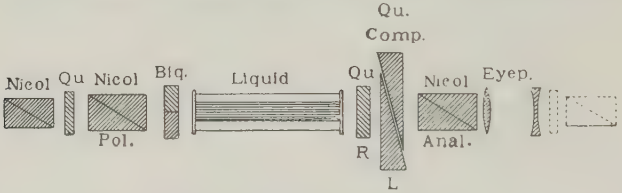


FIG. 798.—The Soleil Polarimeter.

as the rotation of sugar solutions, in the more ordinary strengths used, is comparable in the order of its amount to that of quartz in the thicknesses used; one decimetre of a 50 per cent. sugar solution, for instance, gives + 33·6° of rotation, as compared with 17·3° for a plate of quartz one millimetre thick, both for red C-light.

Spectroscopic Analytical Method of Determining the Rotation Angle.—The most accurate method of all, however, is to analyse spectroscopically the light proceeding from the arrangement of apparatus with a biquartz as recommended on page 1088. By means of a lens of suitable focal length, *r* in Fig. 794, page 1087, a real image of the biquartz is thrown on the slit *v* of the spectroscope, so as to produce one above another two spectra in the field of view of the telescope of the latter, one from each half of the biquartz, which should obviously be arranged for this determination with its diametral cementation-line horizontal. Each spectrum will then be found to exhibit a dark band corresponding to the colour extinguished by the analysing Nicol. On rotation of the latter the two bands will move through the spectra in opposite directions, and the object is to arrange the Nicol so that they are exactly one above the other in the same straight line. When this is achieved it will be clear that light of the same wave-length has been extinguished in the two halves of the field, and that the plane of vibration of the Nicol analyser is parallel to the plane of vibration of the light leaving the crystal-plate. The biquartz may, however, be eliminated as an alter-

native method, when a band or bands will be seen in the spectrum corresponding to the radiations extinguished by the crystal-plate itself.

If sunlight be used and the solar lines clearly focussed, the position of the analyser, and therefore the angle of rotation of the crystal, can be read off for the coincidence of the dark band with each of the principal Fraunhofer lines, such coincidence being brought about by rotation of the analysing Nicol to the necessary extent. The band effects its passage through the spectrum from red towards violet as the analyser is rotated more and more from the original crossed position. If the dispersion of the angle of rotation exceeds 180° for the two ends of the spectrum, but is less than 360°, two bands will appear in the spectrum, and an additional band for every 180° of dispersion. In fact the spectral band or bands never disappear, but simply move along the spectrum in one direction or another, according to the direction of rotation of the analyser and the character of the rotation, right- or left-handed, of the substance under investigation.

The apparatus recommended on pages 1086-1088 serves, when differently disposed, admirably for this spectroscopic method. For the monochromatic illuminator described in Chapter XLIV., employed to supply the polariscope with the necessary monochromatic light, as shown in Fig. 763 (page 1046), is also an excellent spectroscope. It is only needful to replace the fitting containing the ground-glass diffusing screen in front of the exit slit, shown as thus removed at ϕ in Fig. 794, by one of the observing eyepieces χ, in order to convert it at once into an ordinary spectroscope, just, in fact, as it is used during the calibration of the instrument for the passage through the exit slit of monochromatic light corresponding to specific wave-lengths. The exit slit merely requires to be opened wide, with the aid of the adjusting screw ψ, in order that the whole field of the eyepiece may be filled with the spectrum. The large dispersion of the single prism ω of colourless special-flint glass, which has the merit of transmitting a very perfect violet end although so highly dispersive, is particularly suitable for this analytical purpose. The disposition of the whole apparatus is shown in Fig. 794, and it is of perfectly general application, whatever may be the nature of the optically active substance which it is desired to investigate. Sunlight is, of course, used, reflected into the polarising tube i from an adjustable mirror (such as t in Fig. 761, page 1043), which receives its light from a heliostat if one be available; if not, the mirror merely requires periodic further adjustment as the sun gets off the instrument.

Determinations of the Rotatory Power of Quartz. — Accurate determinations of the rotation of quartz have been made by Broch,[1] by von Lang,[2] by Soret and Sarasin,[3] and by Lowry.[4] Broch [1] was the first to use the spectroscopic method, and devised it for the determination of the rotatory power of quartz. His apparatus consisted only of (1) a polariscope, the quartz plate cut perpendicular to the axis being placed in a movable diaphragm between the two Nicols, (2) a slit at some distance

[1] *Ann. chim. phys.*, 1852, *34*, 119. [2] *Wien. Akad. Ber.*, 1876, *74*, 209.
[3] *Arch. Soc. phys. et nat. Genève*, 1882, *8*, 5, 97, and 201.
[4] *Phil. Trans.*, 1912, A, *212*, 261.

from the polariser, and (3) a refracting prism and telescope after the analyser. The Nicol analyser was first arranged exactly at 90° to the polariser, for perfect production of the dark field, in the absence of the quartz plate ; then, after introducing the latter precisely perpendicularly to the axis of the Nicols, exact coincidence of one of the dark interference bands with one of the Fraunhofer lines was brought to occur by rotation of the analyser. Broch used many plates of quartz of very diverse thicknesses, and both right- and left-handed. He was able to determine the angle of rotation for any specific Fraunhofer line to about ten minutes of arc.

Von Lang (*loc. cit.*) subsequently endeavoured to render the two operations, just specified as concerned in a determination, of equal facility and value, by the use of a double-prism or block of the nature of biquartz, and production of two spectra one above the other from the two halves ; the method is that illustrated in Fig. 794, except that no substance plate other than the biquartz was employed, this double-block of quartz serving both as substance plate and biquartz, the material being quartz in both cases and duplication being thus unnecessary. By rotation of the Nicol analyser the interference bands in the two spectra were made to move in opposite directions, until for a certain position of the Nicol they stood identically over each other. The analyser was then rotated first to the right and then to the left, until first in one spectrum and then in the other the nearest interference band coincided with a certain Fraunhofer line. When ψ_1 and ψ_2 are the corresponding azimuths of the Nicol, the angle of rotation ρ for this line is afforded by the formula :

$$\rho = m90° \pm \tfrac{1}{2}(\psi_1 \sim \psi_2),$$

where m is a whole number easily obtained from the thickness of the plate and preliminary determinations. The + sign is to be employed when the interference band lies at the first adjustment on the red side of the Fraunhofer line, and the − sign when the band lies on the blue side. The angle of rotation is in this manner afforded by the difference of two similar observations.

Von Lang found the usual 3·75-millimetres biquartz too thin for his purpose, the bands afforded being too broad. He used, therefore, a double block of right- and left-handed quartz 33·4 millimetres in length, in the direction of the optic axis, along which the light travelled. The exact length was arranged so that the sodium D-line should be practically opposite two coincident bands in the two spectra at the first adjustment of the Nicol, so as to render $\psi_1 - \psi_2$ very small. Such a thick biquartz has to be arranged very near to the slit of the spectroscope, so that the plane of separation of the two halves may bisect the slit. The polarising Nicol was consequently the only one in front of the spectroscope, and was made in von Lang's apparatus the rotating one carrying the divided circle. The second Nicol was fixed in the telescope tube. In order to determine the influence of temperature on the angle of rotation von Lang also enclosed his biquartz in a heating apparatus furnished with plate-glass windows through which the light passed. The maximum error in von Lang's determinations did not reach the one-hundredth of a degree. He found that the temperature change is represented by the following formula :

$$\rho = \rho_0(1 + 0{\cdot}000149t),$$

where ρ and ρ_0 are the angles of rotation at $t°$ and 0°.

Sohncke afterwards showed that this two-term formula is only correct for the mean effect between 20° and 100°, and that the rotation is not constant, but alters with the temperature in accordance with the three-term formula :

$$\rho = \rho_0(1 + 0{\cdot}000\ 099\ 9t + 0{\cdot}000\ 000\ 318t^2).$$

Soret and Sarasin [1] employed the method of Broch with greater refinements, and used no biquartz, merely a much longer prism of simple right- or left-handed quartz

[1] *Arch. Soc. phys. et nat. Genève*, 1882, *8*, 5, 97, and 201.

parallel to the axis. They used the apparatus shown in Fig. 799, in which *a* is a brass tube supported by trunnions on a pair of columns *b*, and adjustable for altitude by means of a divided circle *c*. At the right end the tube carries a polarising Nicol *d* provided with a divided circle *e*, and manipulated by the observer at the spectroscope by means of a shaft *f* and pulley gear *g*. The quartz block *h* is supported in a diaphragm *k*, and a similar diaphragm *l* carrying rectangularly a couple of rods *m* and a plate *n* afford a simple means of effecting the necessary adjustment of the quartz. The analysing Nicol is carried by the rotatable divided circle *o*, which was large enough to read to minutes with the aid of a vernier; it was mounted independently, in a manner which provided it with elaborate adjustments, on the two columns *p*. It was arranged fairly close to the slit *q* of the spectroscope, of which latter *r* is the collimator with its objective *s*, and *t* the telescope, with its eyepiece *u* and objective *v*. The 60° dispersing prism *w* was of Iceland spar in certain of the experiments, cut so that the rays at minimum deviation travelled along the optic axis with only single refraction; in other determinations it was constructed of white flint glass. The glass Steinheil achromatic lenses in many of the experiments were replaced by a complete quartz train, which enabled the observations to be continued into the ultra-violet region of the spectrum. Sunlight was reflected into the apparatus by a heliostat, a quartz lens of 1·4 metres focal length being used to produce an image of the

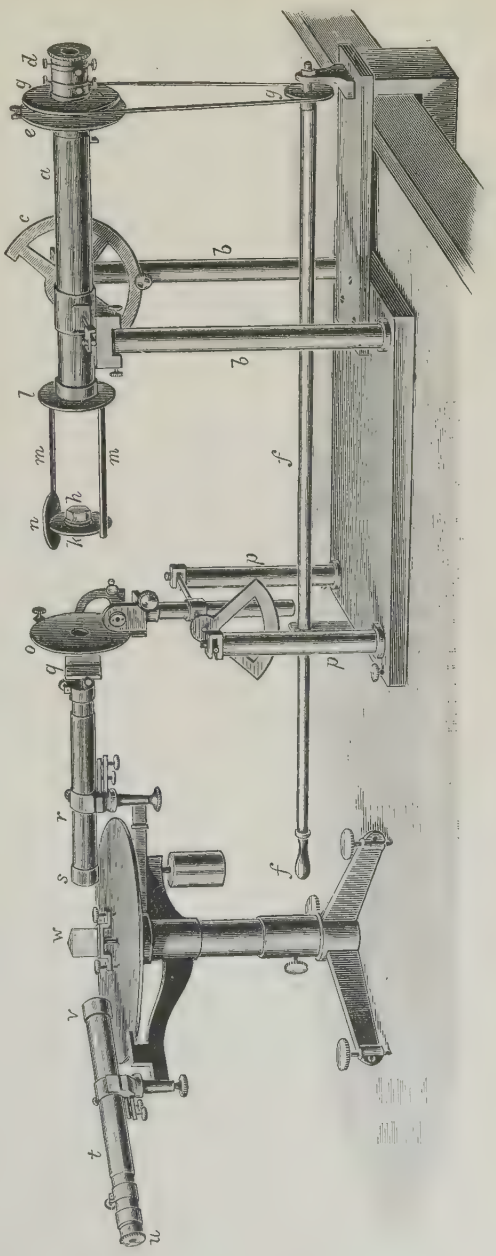


FIG. 799.—Apparatus employed by Soret and Sarasin for the Determination of the Optical Rotation of Quartz.

sun on the slit of the spectroscope. Two quartz blocks were found most satisfactory among a large number used; one was of 30 millimetres thickness, and of left-handed quartz, and the other was of right-handed quartz and no less than 60 millimetres thick. Both were single crystals, no biquartz being employed by Soret and Sarasin, and the ends were truly plane and parallel to each other, and perpendicular to the optic axis, which direction it was most carefully arranged should be traversed by the rays during the determinations.

In some further measurements with monochromatic light Soret and Sarasin (*loc. cit.* p. 201) employed the method of the Laurent saccharimeter, the essential point of which has already been shown to be that precision in the angular measurement of the position of the analysing Nicol is attained by the use of a half-shadow plate, which is a plate of glass half covered by a half-wave plate of quartz, gypsum, or mica. The plane of polarisation, with or without the plate of rotatory substance under investigation (quartz in the experiments under consideration), is determined by turning the analyser until the two halves of the Laurent plate show equality of illumination. With sodium light, and using quartz for the half-wave portion of the composite plate, this method of Laurent proved likewise very satisfactory in the hands of Soret and Sarasin.

Lowry [1] employed an elaborate spectroscopic method, for the details of which the original memoir should be consulted, and which involved the essentials, with additions and modifications, of the apparatus devised by Sir William Perkin for his well-known researches on magnetic rotation (rotation of the plane of polarisation of light by substances placed under the influence of a magnetic field, a phenomenon discovered by Faraday in the year 1846). The determinations were made for 24 wave-lengths of light, by employing the metallic bright-line spectra of sodium, lithium, thallium, mercury, cadmium, silver, zinc, and copper with columns of dextro- and lævo-quartz 181·44 and 226·37 millimetres in length respectively, each made up of 4 cylinders parallel to the optic axis and arranged successively in optical contact. The lævo cylinders afforded as the final result a rotation of 25·5371° per millimetre for the mercury green line (wave-length 0·0005461mm.) and the temperature of 20° C. The dextro column afforded the rotation of 25·5361°. The results are thus very satisfactorily concordant.

The angles of rotation ρ for a plate of quartz one millimetre thick, at the temperature of 20° C., for light of the wave-lengths of the principal Fraunhofer lines, as derived from these four series of measurements by Broch, von Lang, Soret and Sarasin, and Lowry, are given in the following table:

Rotation Angles of Quartz 1 mm. thick at 20°.

Solar Line.	Broch.	Von Lang.	Soret and Sarasin.	Lowry.*
A	..	..	12° 39′ = 12·65°	..
B	15° 18′ = 15·30°	..	15 45 = 15·75	..
C	17 14 = 17·24	17° 18′ = 17·30°	17 19 = 17·31	..
D	21 40 = 21·67	21 44 = 21·73	21 41 = 21·69 D_1	21° 42′ = 21·70° D_1
			21 44 = 21·73 D_2	21 45 = 21·75 D_2
E	27 28 = 27·46	..	27 32 = 27·54	..
F	32 30 = 32·50	32 43 = 32·72	32 46 = 32·76	..
G	42 12 = 42·20	..	42 35 = 42·59	..
H	..	..	51 11 = 51·19	..

* In the original memoir (*loc. cit.* below) the values for 22 other metallic lines are given.

[1] *Phil. Trans.*, A, 1912, *212*, 261.

Further Colour Phenomena of Quartz due to its Optical Activity, and Discrimination of the Two Varieties.—Right- and left-handed quartz are readily distinguished by the order of succession of the colours on rotating the Nicol analyser, from the crossed position with respect to the polariser. A right-handed crystal becomes first red, then orange, yellow, green, blue, and violet, as the analyser is rotated in the direction of the hands of a watch, from the point of view of the observer looking in the same direction as the light is being propagated; whereas a left-handed crystal gives this order on rotating the analyser anti-clockwise. The two varieties are also distinguished by the manner of movement of the circular rings, afforded in convergent polarised light by a plate perpendicular to the axis, when the analyser is rotated. The usual black cross of a uniaxial figure is absent from the centre of the figure afforded by a plate of quartz perpendicular to the axis, of the thickness required to produce several rings, although the arms of the cross appear towards

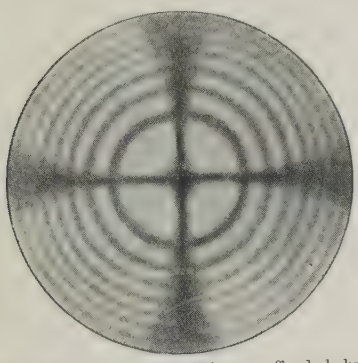


FIG. 800.—Interference Figure afforded by Quartz Plate 1 mm. thick in strongly Convergent Polarised Light.

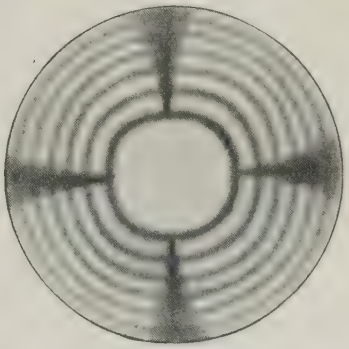


FIG. 801.—Interference Figure afforded by Quartz Plate 3·75 mm. thick in moderately Convergent Polarised Light.

the margin of the field; this is owing to the rotatory polarisation, indeed, the disappearance of the cross is the more complete the thicker the section-plate. Moreover, the centre is never black, but coloured just as the whole plate would be in parallel light. The succession of colours at the centre, on rotating the analyser, will thus be the same as that just given for parallel light. A plate one millimetre thick, however, which has already been shown to afford only weak colours in parallel light, and only exhibits a very few widely separated rings in the usual field, and using the same convergent system of lenses as that convenient for the thick plate, does show the black cross. A photograph of such a figure, but using a more strongly convergent beam, is reproduced in Fig. 800. A right-handed or left-handed quartz plate, of 3·75 mm. thickness, affords an interference figure such as that reproduced from an actual photograph in Fig. 801.

On rotating the analyser from the crossed position in the direction of the hands of a watch (regarded, as stated on the previous page, in the direction in which the light is travelling), the rings of such a quartz figure

as Fig. 801 expand when the crystal plate is right-handed, and contract if the section has been cut from a left-handed crystal, as they change to produce the figure for parallel Nicols, the central ring also becoming nearly square. When such an equally thick pair of right- and left-handed plates are superposed, a double spiral figure is produced, the well-known "Airy's Spirals," photographically reproduced in Fig. 802 as afforded by the pair of plates one of which was used for Fig. 801.

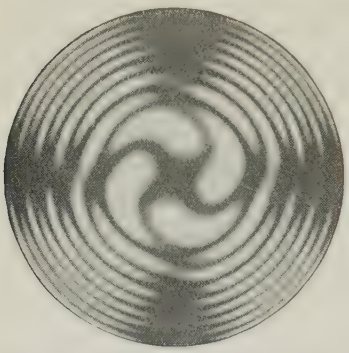


FIG. 802.—Airy's Spirals obtained by Superposition of a Right-handed and a Left-handed Plate of Quartz 3·75 mm. thick in moderately Convergent Polarised Light.

It is of considerable theoretic interest that Reusch has succeeded in artificially reproducing these figures for right- and left-handed quartz, by arranging an adequate number of strips of mica films over each other in a clockwise and anti-clockwise manner respectively; and that a pair of these imitation quartzes of mica, of opposite rotations, also reproduce Airy's spirals when placed over each other between crossed Nicols. In each of Reusch's preparations obtained from Messrs. Steeg & Reuter of Homburg 24 lamellæ are laid over each other at angles of 60°, thus making four complete screw turns. The arrangements are indicated in Figs. 803 and 804, the numbers indicating the order of the laying down of the strips.

Regarding them from above, as laid on the stage of the polariscope, which is the opposite way to that in which the polarised light from the polarising Nicol meets them, the right-handed preparation has the strips arranged in anti-clockwise order, or clockwise to the rays of incident light; while the left-handed preparation has the strips arranged clockwise, or anti-clockwise to the incident light rays. All the lamellæ are taken from the same cleavage sheet of mica of equal thickness throughout. One-eighth-wave thickness of mica-film is the best for the purpose. The direction of the line joining the optic axes is diametral in all the 24 strips, that is, parallel to the longer edges of the

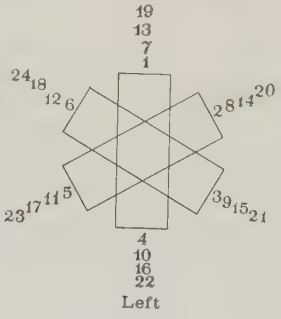


FIG. 803.

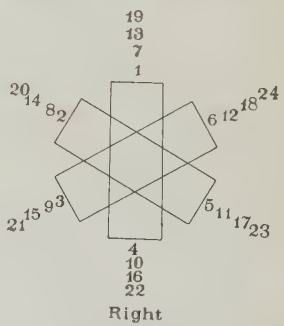


FIG. 804.

Reusch's Simulated Left- and Right-handed Quartzes composed of spirally arranged Mica Films.

strips. Hence, this direction is rotated four times during the passage of light through all the 24 films.

These two mica preparations, artificial quartzes, are obviously the mirror-images of each other, and form a splendid proof of the mirror-image or "enantiomorphous" similarity of the two varieties of quartz.

Striking Screen Demonstration of Right- or Left-handed Character of Quartz.—A very beautiful screen experiment, due to S. P. Thompson, for exhibiting the right- and left-handed rotations of the two varieties of quartz in a striking manner is as follows: A circular plate is prepared, composed of 24 sectors of half-wave mica, all cut from the same half-wave film and in such a manner that the direction of the line joining the two optic axes of the mica bisects each sector; this direction is consequently radially arranged when the composite plate is complete. The 24 sectors are carefully cemented closely side by side radially, with their points at the common centre, with hard balsam in benzene (or better, turpentine, the drying then more probably occurring without bubbles), on a circular glass plate of the usual $1\frac{7}{8}$-inch diameter for projection purposes in parallel light. When the balsam has set, some days subsequently, a second glass plate is likewise cemented over them, so as to enclose the sectors permanently in balsam between the two protective glass plates. When the whole is hard the composite plate is mounted in the usual rectangular mahogany frame with rabbeted 2-inch circular aperture, in which it is maintained by a brass spring-ring; it should be arranged so that the bisecting line of one pair of sectors is vertical when of course that of another pair will be horizontal. On placing it as a polarising object on the stage of the projection polariscope, exactly as shown in Fig. 633 on p. 853, and under crossed Nicols, it affords, on actuating the arc of the lantern, the appearance on the screen which is shown in Fig. 805 and on a smaller scale at *a* in Fig. 806, the shading lines indicating the direction in each sector of the line joining the optic axes. The vertical and horizontal sectors are at extinction, and appear as a black cross, while the sectors occupying the diagonal 45°-positions are brilliantly white; the intermediate sectors show regularly varying tones of grey, the whole being a very beautiful object of exquisite shades of French grey, passing in each quadrant into jet black at the vertical and horizontal positions and into white at the bisecting 45°-positions.

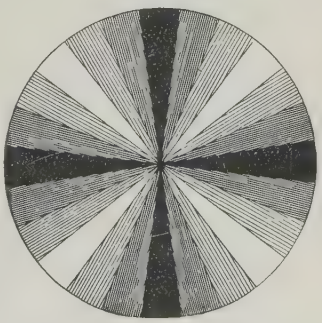


FIG. 805.

When now a right-handed plate of quartz 1 mm. thick cut perpendicularly to the axis is introduced normally into the beam, that is, parallel to the mica plate, preferably behind the latter, the black cross rotates one sector to the right, as shown at *b* in Fig. 806, and a little colour of delicate shades is introduced into the whole figure. When, on the other hand, a left-handed one-millimetre plate is introduced, the black cross

rotates one sector to the left, as shown at *c*. The experiment is very striking if the two quartz plates are mounted independently in the same carrier frame, so that they can be rapidly inserted in succession or alternated; the rotation of the cross is then particularly marked, first to one side and then back through two sectors to the other, according to the right- or left-handed character of the plate introduced. This thin carrier frame, $5\frac{7}{8}$ by $2\frac{5}{8}$ inches, of hard mahogany, containing side by side the two

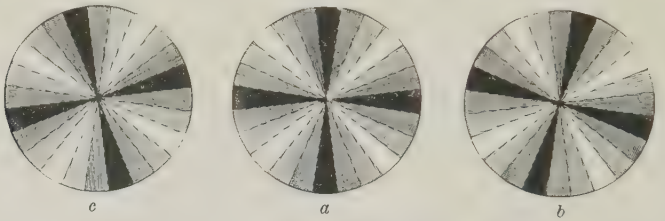


FIG. 806.—Demonstration of Right and Left Rotation of Quartz.

oppositely rotating quartz plates each 1 millimetre thick and 2 inches in diameter (between opposite corners of the hexagon, that of the hexagonal prism from which each was cut), is arranged to slide easily in a supporting mahogany frame carried like a second stage immediately behind the rotating object stage (which in this experiment carries the mica sector-plate), shown in Fig. 634 (page 855) but not shown in Fig. 633. This second stage forms the upper part of an upright, easily removed when not required, attached in a steady, dovetailed manner, to the adequately deep base of the object stage. The two stages are thus brought very close to each other. A greater thickness of quartz than one millimetre is a disadvantage, as the black cross begins itself to colour and to lose its distinctive and striking character. The carrier frame with this pair of quartz plates is also shown in Fig. 634, on the plinth.

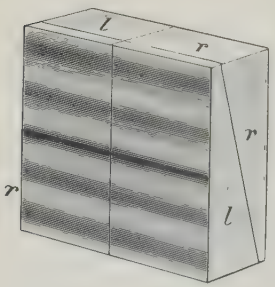


FIG. 807.—Four-wedge Biquartz, and Effect produced by it under Crossed Nicols.

The Four-wedge Biquartz.—A form of biquartz which also affords a striking method of demonstrating optical rotation on the screen, and which is also used sometimes in determinations of rotation, when the spectroscopic analytical method is not adopted, consists of a compound rectangular block made up of four equal wedges, composed of the two varieties of quartz, alternately arranged as shown in Fig. 807. The wedges marked *r* are of right-handed quartz, and those marked *l* of left-handed. Each rectangular half, composed of two wedges of opposite rotation, affords in the dark field of the crossed Nicols a black band in the central line, where the thickness of the two wedges is the same and the rotations in opposite directions exactly neutralise each other. On each side of this central band, separated by a narrow interval illuminated with white light, are a series of spectrum-coloured bands at regular intervals, corresponding

to the orders of Newton, due to the regular increments of thickness and consequently preponderating amount of rotation of one wedge over the other. On cementing the two blocks together as one block like a biquartz, inverted as regards the front and back positions of the right- and left-handed wedges, as shown in Fig. 807, and again placing between crossed Nicols, the two sets of bands are observed to be exactly in line with each other, and the black central line of one to form a continuation of that of the other, when the analyser is exactly crossed to the polariser. But on the slightest rotation of the analyser, or on the introduction into the optical system of a plate of a rotating substance, the bands move in opposite directions, and the angle through which the analyser has to be rotated in the latter case, in order to restore the two halves of the black band to the same straight line, is the measure of the angle of rotation of the crystal-plate.

The Biot Quartz Plate.—A sensitive quartz plate of 3·75 millimetres thickness, cut perpendicularly to the axis, is also often used in crystal microscopy, instead of the sensitive gypsum plate giving an even red of the first order referred to in Chapter XLII. page 899, and is known as a "Biot quartz plate." As shown on pages 1082 and 1083, it exhibits the blue-violet transition tint when the Nicols are parallel, and an even yellow when the Nicols are crossed. It is generally inserted over the objective as a slider in a slot of the optical tube of the microscope, between the polariser and analyser. For as it changes so rapidly into red of the first order or blue of the second order (with parallel Nicols), or into orange or green (with crossed Nicols), when the doubly refractive effect of another thin crystal is superposed, it is most useful for determining the sign of the double refraction of microscopic crystals, by the sense in which the colour changes as the stage is rotated towards the 45°-position of the planes of vibration of the small crystal, with respect to those of the crossed or parallel Nicols, the uniform tint of the quartz being interrupted by the higher or lower order colour of the crystal.

Discrimination between the Double Refraction Interference Colours of Quartz and Colours due to Dispersion of Optical Rotation.—It was stated in Chapter XLII. (page 903) that quartz, when examined in very thin plates under the microscope, is one of the most brilliantly polarising of crystals, owing to interference due to double refraction. For this reason it is readily recognised in rock sections, the usual thickness of which is about 0·04 millimetre. A quartz section-plate of approximately this thickness affords brilliant first or second order double refraction colours under crossed Nicols, when the plate is not perpendicular to the optic axis or nearly so (when extinction occurs under crossed Nicols), and when the vibration directions are in the neighbourhood of 45° to the planes of the Nicols. As the thickness increases the colours pale off as described in Chapter XLII., more and more white light becoming admixed until after the seventh order of spectrum colour has been passed we have first the "white of the higher orders," and eventually pure white light. But when the thickness approaches a millimetre the rotation colours begin to be clearly visible, although weak, if the direction of the section-plate be not too far from normal to the optic axis, due to the other

phenomenon of optical activity, and for a plate of 3·75 mm., as we have seen, these colours are brilliant, and particularly so when the plate is actually normal to the axis. This is even more so when the double thickness of 7·5 mm. is reached. Hence, we have the two distinct sets of colour phenomena to discriminate between in the case of quartz, both brilliant, that due to double refraction in very thin plates, and which attains its maximum in a plate parallel to the axis; and that due to optical activity in thick plates, which is most intense when the plate is perpendicular to the axis. It is this latter attribute of quartz, of polarisation in thick plates, which renders it so magnificent a subject for screen experiments with the lantern polariscope, large and thick plates of quartz being exceedingly valuable for this purpose.

Interference Bands in Quartz by combined Scattering and Rotation of Light.—A beautiful series of experiments on the scattering of light by quartz, in which the optical rotation of the crystal plays a conspicuous part, have been carried out by Prof. the Hon. R. J. Strutt[1] (now Lord Rayleigh). Yellow quartz and smoky quartz possess the property of scattering light very strongly, the foreign colouring matter being evidently distributed in the crystal in the form of small particles. The quartz crystal is best cut into a rectangular block, if possible two or three inches in length and an inch or more in the two other dimensions, with the longest edges parallel to the optic axis of the crystal. When a narrow parallel beam of light about 6 mm. diameter from the condenser of an electric lantern is sent along the axis the scattering is very clear, the beam being rendered strongly visible by it. Moreover, the light is polarised, and of a distinctly bluish colour.

In previous experiments on the scattering of light in glass, it had been found that the scattered light was always polarised and bluish, the depth and purity of the blue being a measure of the completeness of the polarisation. Vibrations parallel to the direction of the primary beam afforded a weak image on examining through a Nicol prism with its vibration direction parallel to the beam, while on rotating the Nicol 90° a very much stronger image of the block and beam were observed, composed of vibrations perpendicular to the primary beam. The intensity of the weak image was from 3 to 8 per cent. only of that of the strong image. The scattering in glass is regarded as also being due to minute particles of impurities rather than to molecules.

In the case of yellow quartz from Madagascar and smoky quartz from Brazil, the polarisation was more complete, the weak image in the latter case being never more than three *per cent.* as intense as the strong image, and in the former case it was of less than the hundredth part of the intensity of the strong one, the vibrations of which were perpendicular to the axis. This strong image was coloured a rich sky-blue in the latter case, and in the case of the weak image from the yellow quartz the blue was even purer and deeper, resembling the "residual blue" observed by Tyndall in precipitated clouds, when the particles were small compared with the wave-length.

[1] *Proc. Roy. Soc.*, A, 1919, *95*, 476.

If now the block be turned so that the primary beam travels perpendicularly to the axis, and the observer looks along the axis, then the rotatory property of the crystal comes into play, and the two polarisations appear of equal intensity, owing to several complete rotations having been caused by the great thickness of quartz used. The most beautiful of the experiments, however, is afforded when a Nicol is employed to polarise the incident beam, the cloud of particles themselves then acting as analyser. As the beam advances along the axis into the crystal the plane of polarisation is rotated, so that alternations of light and darkness are observed laterally, corresponding to rotations of 90°. In white light the rotatory dispersion gives striking coloured bands, similar to interference bands, and like them losing purity after a few bands owing to the superposition of the different orders. Visually five or six bands can be traced, but photographically several more are revealed, as reproduced in Fig. 808. Another reproduced photograph in Fig. 809 represents the appearance in monochromatic violet light from a quartz mercury lamp, corresponding to the violet line of mercury.

FIG. 808.—In White Light.

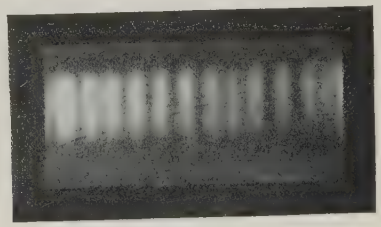


FIG. 809.—In Violet Mercury Light.

Interference Bands in Quartz by Scattering and Rotation.

A particularly pretty effect is obtained when a polarised beam is passed in succession through two crystals, the first right-handed and the second left-handed, the latter being twice the length of the former. Using white light the bands appear with maximum distinctness where the beam enters the first crystal, becoming fainter along the length of this crystal according to the rule already referred to. The second crystal, however, reverses the action of the first, and the bands become more distinct again, until the beam has traversed an equal thickness of each, that is, until it reaches the middle of the second crystal. Here the planes of polarisation for the various colours again coincide, and maximum distinctness is recovered. Beyond this the bands gradually fade out again. Thus the central white band occurs in the middle of the second crystal, with the coloured bands ranged in descending order of intensity on each side of it. The appearance is the same as that of the complete interference fringes in white light produced by Fresnel's biprism or any equivalent device. On rotating the polariser the bands travel along the axis in opposite directions. To get the bands in their full intensity, it is important to adjust the crystals so that the light traverses the optic axis of both crystals with fair accuracy.

Pure colourless quartz has only a very slight scattering effect, usually

not perceptible to the eye, but revealed by photography. The scattering by this clear quartz is, however, about eight times as strong as that of dust-free air. Clear Iceland spar also gives a scattering strong compared with air, although very weak compared with yellow or smoky quartz. It would appear to have been proved by Prof. Strutt that in all the cases of quartz and calcite studied, the scattering has only relation to the foreign enclosures, however minute, and not to the atomic or molecular crystal structure. Only X-rays are competent, by virtue of their short wave-length being of the minute order of atomic dimensions, to be scattered by the actual units, the atoms building up the crystal structure, and this is specially dealt with in Chapter XXXIII.

Other Optically Active Crystalline Substances.—Quartz is relatively powerful as an optically active substance, and in order to form a true perspective of the subject it is necessary to compare its rotatory power with that of other active crystalline substances. Another very prominent substance also endowed with the property is sodium chlorate, $NaClO_3$, and in this case it is only developed to a typically low degree. In the following table the angles of rotation for a plate of sodium chlorate one millimetre thick, as determined by Guye, are given for the same wave-lengths, those of the prominent Fraunhofer lines, as those for quartz already tabulated on page 1100.

Angles of Rotation ρ for Sodium Chlorate.

Fraunhofer line	B	C	D	E	F	G	H
Rotation angle	2° 16′	2° 30′	3° 8′	3° 56′	4° 40′	6° 0′	7° 10′

The two oppositely optically active varieties of both quartz and sodium chlorate exhibit equal amounts of the two opposite rotations, so that the angles ρ are identical for the two varieties, but the signs are different. The reason is that in the crystals of one variety, the right-handed, the clockwise circular movement or vibration is the more rapid, whilst in the other modification, the left-handed, the anti-clockwise orbital movement is the quicker. With equal thickness of plate, however, the amounts of rotation exhibited by the two varieties are exactly equal, corresponding to their exact mirror-image symmetry. The structure of sodium chlorate and bromate has been determined by N. H. Kolkmeyer[1] by the X-ray method of Debye and Scherrer. The elementary cube cell contains four molecules of $NaClO_3$, and its edge is $6{\cdot}55 \times 10^{-8}$ cm. for sodium chlorate and $6{\cdot}74 \times 10^{-8}$ cm. for sodium bromate. This unit cell is divided into eight smaller cubes, four of which, chosen tetrahedrally, each contain one molecule, and the sodium and halogen atoms are situated on non-intersecting diagonals of the four cubes. The three oxygen atoms are grouped around a halogen atom, at a distance from it of one-seventh of the parameter of the lattice. This structure would appear to agree with the enantiomorphous nature of class 28.

The more important substances the crystals of which rotate the plane

[1] *Proc. Kon. Akad. van Wetensch.*, Amsterdam, 1920, *23*, 644.

of polarisation of light are arranged below according to their symmetry, and the amounts of their rotation for yellow sodium light (except in the case of cinnabar, for which the only available determination is for red light), for a plate 1 mm. thick, are appended.

Cubic System.

Tetrahedral-pentagonal-dodecahedral class (cubic-tetartohedral), Class 28.

	$\rho_{Na.}$		Observer.
Sodium chlorate, $NaClO_3$	3°	8′	Guye
„ bromate, $NaBrO_3$	2	10	Traube
„ sulphantimoniate, $Na_3SbS_4 . 9H_2O$ (Schlippe's salt)	2	40	Marbach
„ uranyl acetate, $NaUO_2(C_2H_3O_2)_3$	1	29	Traube

Tetragonal System.

Trapezohedral class (trapezohedral-hemihedral), Class 11.

Hydrogen Zinc malate, $Zn(C_4H_5O_5)_2 . 2H_2O$	3°	1′	Traube
Strychnine sulphate $(C_{21}H_{22}N_2O_2)_2 . H_2SO_4 . 6H_2O$	13	15	„
Ethylene diamine sulphate, $C_2H_4(NH_2)_2 . H_2SO_4$	15	30	von Lang
Guanidine carbonate $(CN_3H_5)_2 . H_2CO_3$	14	34	Bodewig
Diacetyl phenolphthalein, $C_{20}H_{12}O_4(C_2H_3O)_2$	19	42	„

Hexagonal System.

Hexagonal-pyramidal class (hemimorphic-hemihedral), Class 23.

Potassium lithium sulphate, $KLiSO_4$	3°	26′	Traube

Trigonal System.

Trapezohedral class (trapezohedral-tetartohedral), Class 18.

Quartz, SiO_2 (see special table)	21°	44′	Lowry
Rubidium dextro tartrate, $Rb_2C_4H_4O_6$	10	12	Traube
Cæsium dextro-tartrate, $Cs_2C_4H_4O_6$	19	0	„
Potassium dithionate, $K_2S_2O_6$	8	23	Pape
Lead dithionate, $PbS_2O_6 . 4H_2O$	5	32	„
Calcium dithionate, $CaS_2O_6 . 4H_2O$	2	6	„
Strontium dithionate, $SrS_2O_6 . 4H_2O$	3	23	„
Benzil, $C_6H_5 . CO . CO . C_6H_5$	25	0	Des Cloizeaux
Cinnabar, HgS, most powerfully rotatory substance known, 20 times as great as quartz	325° for red light		„

Pyramidal class (hemimorphic-tetartohedral), Class 16.

Sodium periodate, $NaIO_4 \cdot 3H_2O$	23°	18′	von Groth

In the cases of the cubic and therefore isotropic crystals of the first four substances mentioned in the list, the rotation is the same in all directions, the angle only varying with the wave-length of the light and the thickness of the plate. The latter may be cut out of the crystal in any direction. The crystals of the remaining substances in the list, all of which are optically uniaxial, only show the pure phenomenon of

rotation of the plane of polarisation in the direction of the optic axis, the plate for investigation being in all cases cut perpendicularly to the optic and principal crystallographic axis. For only along this direction is there no double refraction to complicate the phenomenon, the crystal behaving as if isotropic along this direction of the axis. Hence, all the measurements of rotation given in the list, except those for the 4 cubic substances, refer to the axial direction.

The moment the inclination of the plate to the optic axis commences to vary from 90° the influence of double refraction begins to be manifest. A plate of quartz cut parallel to the axis, in fact, shows with light of ordinary intensity no sign of rotatory power, the interference phenomena being apparently entirely those due to double refraction. Airy, Gouy, and Wiener have shown that as the inclination to the axis alters from 90° the circular orbits of the vibrations become elliptical, and finally, as parallelism to the axis is attained, these become converted into truly linear vibrations. Voigt has shown, however, that it is impossible absolutely to extinguish the light when very intense, with a plate parallel to the axis. But speaking in general terms, and as regards readily observable phenomena, it has been clearly demonstrated experimentally by Airy that elliptic vibrations are really produced by sections inclined at angles other than 90° to the principal axis, and he actually determined the precise dimensions of the axes of the ellipse, and the complete form of the vibrations. Jamin added to this information knowledge concerning the relative retardation of the two series of elliptic vibrations behind one another, and Hecht further confirmed the complete agreement of observation with theory. Later Croullebois and MacConnel also determined the difference of path traversed by the elliptic vibrations. Croullebois went so far, indeed, as to render the two elliptically vibrating rays separately visible, by means of a double-prism of a similar character to that of Fresnel shown in Fig. 785, page 1080, only composed of two simple prisms of 82° angle, of right- and left-handed quartz respectively, and cemented together by their hypotenuse faces, and with the further difference that the rectangular entrance and exit faces were inclined 80° to the optic axis instead of being normal thereto. Later work by Brunhes, Beaulard, and Voigt, and a masterly analysis of the whole subject by Pockels, have resulted in the perfect establishment of these facts, in exact accordance with the theory of the superposition of the effects of double refraction of the ordinary linear-vibration kind on the phenomena of circular polarisation, as the direction of the optic axis of a uniaxial crystal is departed from.

The question of possible OPTICAL ROTATION on the part of BIAXIAL CRYSTALS is a very difficult one, as there is no direction of absolute single refraction, along which the phenomena can be observed uninfluenced by double refraction effects. The two optic axes have been shown in Chapter XLI. to be only the optic binormal approximations to true directions of single refraction for a specific wave-length. The case of cane sugar, $C_{12}H_{22}O_{11}$, belonging to the sphenoidal class 4 of the

monoclinic system, has, however, been investigated by Pocklington,[1] and the dark centres of the hyperbolic brushes marking the two optic axes found to exhibit rotation, only becoming black on rotation of the analyser from the crossed position, one to the right, that perpendicular to the cleavage direction, and the other to the left, corresponding, for a plate 1 millimetre thick and for sodium light, to $\rho = +2° 12'$ and $\rho = -6° 24'$ respectively. As the optic axes lie in the symmetry plane in the case of crystals of cane sugar, it was to be expected that their rotations would be unequal.

Seignette salt, potassium sodium dextro-tartrate, $KNaC_4H_4O_6 . 4H_2O$, crystallising in the bisphenoidal class of the rhombic system, was also investigated by Pocklington, and for sodium light a plate 1 mm. thick gave $\rho = -1° 12'$ for both optic axes, the two being equal in accordance with rhombic symmetry.

Dufet[2] has investigated three other salts also belonging to the bisphenoidal class of the rhombic system, namely, Epsom salts (magnesium sulphate), $MgSO_4 . 7H_2O$, which gave a rotation of $\rho = +2° 36'$ for a plate 1 mm. thick perpendicular to an optic axis; sodium dihydrogen phosphate, $NaH_2PO_4 . 2H_2O$, which afforded a left rotation of $\rho = -4° 27'$; and ammonium Seignette salt, $Na(NH_4)C_4H_4O_6 . 4H_2O$, which gave a dextro rotation of $\rho = +1° 33'$, although its solution is lævo-rotatory. Dufet also investigated two monoclinic substances belonging to the same hemimorphic (sphenoidal) class as cane sugar, namely, the sugar known as rhamnose, and tartaric acid (the ordinary dextro variety), $C_4H_6O_6$. In the case of the latter, the plane of the optic axes is perpendicular to the symmetry plane, and so the rotations along the two optic axes are equal; they amount to $\rho = +8° 33'$ for Li-light, $11° 24'$ for Na-light, and $14° 14'$ for Tl-light. In the case of rhamnose the optic axes lie in the symmetry plane, so that the rotations for the two are different, namely, $\rho = +12° 54'$ and $\rho = +50° 24'$. As this is a substance of extremely feeble double refraction the optical rotation is very marked.

Karandéev[3] has more recently investigated the optical rotatory power of quercitol, $C_6H_7(OH)_5$, a monoclinic substance the crystals of which were measured by Lewis. As the optic axes lie in the plane of symmetry, the two axes exhibit different amounts of rotation. For plates 1 mm. thick the respective rotations are $-3·5°$ and $-4·6°$. The solution also rotates the plane of polarisation of light, but to the right.

From these facts it will be clear that the phenomenon of rotation of the plane of polarisation of light extends throughout the eleven enantiomorphous classes of crystal symmetry, in accordance with the rules which have been laid down in Chapter IX. page 132.

[1] *Phil. Mag.*, 1901, *2*, 368.
[2] *Journ. de Phys.*, 1904, *3*, 757; *Bull. Soc. Fran. de Min.*, 1904, *27*, 156.
[3] *Bull. Acad. Sci.*, Petrograd, 1915, *9*, 1285.

CHAPTER LI

THE COLOUR OF CRYSTALS, ABSORPTION OF LIGHT, AND PLEOCHROISM—LUMINESCENCE—OPTICAL ANOMALIES

MANY crystals are coloured, and the colour may be due either to minute enclosures of foreign matter, when it is said to be "allochromatic," or to the intrinsic nature of the substance itself when it is termed "idiochromatic." Thus the sapphire and ruby are composed of colourless oxide of aluminium, Al_2O_3, equally with corundum, and chemical analysis is only just able to detect the traces of ferric oxide or chromic oxide, to which the colour is due which renders the ruby and sapphire so valuable as gem-stones. When a ruby is examined in plane-polarised light, under the polarising microscope to be described in the next chapter for instance, with only the polarising Nicol in position, the colour appears deep red in one direction, that in which the ordinary ray ω is transmitted, while if examined in a direction permitting only the extraordinary ray ϵ to escape the colour appears to be a violet red. Likewise the sapphire appears to change colour according to the ray extinguished or transmitted, being deep blue when the ordinary ray is transmitted and greenish-blue when the extraordinary ray is alone allowed to escape. These gems are, therefore, said to be "dichroic," or "pleochroic," and their dichroism is owing to admixture with a minute amount of foreign oxides, modified by the structure of the crystals, which renders them doubly refractive. Allochromatism may be due to two classes of impurities, namely, minute enclosures of particles of coloured foreign substances, as in the cases of the two coloured varieties of corundum just mentioned, or to small quantities of a foreign substance in the state of solid solution, as occurs with many crystals of organic substances, difficult to purify absolutely, or slightly decomposed by light.

On the other hand many crystalline substances are coloured in their own right, due to absorption of light of certain wave-lengths in its passage through the crystal, the beautiful blue crystals of copper sulphate, $CuSO_4 . 5H_2O$, for instance; and if they are birefringent the colour is different for the light corresponding to the two rays travelling through the crystal with different velocities and vibrating parallel to different directions of the crystal, the difference being made particularly manifest when one of them is extinguished by a Nicol prism. Tourmaline is an extreme

case not requiring a Nicol, where one ray (the ordinary) is completely absorbed by the crystal itself, permitting only the other (the extraordinary) which vibrates parallel to the axis of the uniaxial crystal to escape, as fully explained in Chapter XXXVII. (p. 807). It frequently happens, however, that the crystals of a coloured birefringent substance show different colours in different directions, owing to the different selective absorption of light, from the gamut of wave-lengths presented by the visible spectrum, which occurs for the two rays vibrating perpendicularly to each of the different directions of transmission examined, leaving the light actually transmitted tinted complementarily to the colour chiefly absorbed. The subject of the absorption of light by crystals therefore demands careful attention.

Absorption of Light by Crystals.—On passing through a crystal a beam of light in general suffers diminution in intensity by absorption. If the amount be trivial the substance is "transparent," but if it be very considerable the substance is more or less "opaque." Moreover, the absorption differs with the wave-length of the light vibrations, so that the issuing light may be quite differently coloured from the original beam (supposing the latter to be not strictly monochromatic), or if the latter be composed of ordinary white light the issuing light may be coloured. Even if the absorption be small, the quality of the issuing light, although it remains apparently still white, is altered. Again, many substances which appear colourless when examined in thin plates exhibit colour when more considerable thicknesses are employed. Examined spectroscopically, the light from an absorbing substance exhibits absorption bands in its spectrum. No solid or liquid substance is yet known which absorbs all but the light corresponding to a single line and wave-length in the spectrum; that is, pure monochromatic light is not yet obtainable by merely passing ordinary white light through a crystal or other transparent solid, such as glass, or even through any known liquid contained in a parallel-sided cell. Screens of coloured glasses, solutions of dyes in such cells, coloured gelatine films, and other devices, have for long been experimented with, especially by Mr. Sanger Shepherd and Dr. Mees, for photographic purposes; and although some considerable success has been achieved in producing screens which permit to pass only light of a narrow range of wave-lengths, corresponding to a fairly narrow band in the spectrum, it is still essential, in order to obtain absolutely pure monochromatic light, to have recourse to glowing vapours, metallic vapour-flames, such as those of sodium, lithium, and thallium, or of the cadmium or mercury lamp, or to glowing gases in Geissler tubes, such as one containing a trace of hydrogen, or of the rare inactive gaseous element neon, which latter affords monochromatic yellow light corresponding to a single predominating line in the spectrum; or, better still, to employ the universally applicable spectroscopic monochromatic illuminator described in Chapter XLIV. Absorption spectra are indeed generally complicated, consisting of numerous dark bands in the continuous spectrum, of varying depths of blackness and breadth.

It will have been gathered from what has already been said that

idiochromatic crystalline substances only afford identical absorption phenomena, and therefore equal and similar colour, in all directions when the crystals belong to the isotropic cubic system of symmetry. In the more frequently occurring cases of doubly refractive uniaxial or biaxial crystals the absorption phenomena correspond precisely to the symmetry. In general, equal thicknesses of these substances taken from different directions in the crystals show differences both of brightness and of colour, the phenomenon of "pleochroism" already mentioned. The distribution of absorptive power may, in fact, be represented graphically by an ellipsoid of revolution, in the cases of hexagonal, tetragonal, and trigonal crystals; and by an ellipsoid of general form with three unequal rectangular axes, in the cases of rhombic, monoclinic, and triclinic crystals. This ellipsoid is best termed the "Absorptive Surface." It is usually calculated on the assumption that, if a be the absorption coefficient, the ellipsoid is that traced out by lines drawn from the centre of the crystal and of lengths proportional to $\frac{1}{\sqrt{a}}$. It was termed by Mallard the "Ellipsoïde inverse d'Absorption."

The coefficient of absorption a is afforded by the equation

$$I = I' e^{-at},$$

where I is the intensity of the light issuing from the crystal, I′ is that of the incident light, e is the base of Napier's logarithms, and t is the thickness of the crystal. In the case of cubic crystals the ellipsoid of absorption becomes a sphere of different radius for light of different wave-lengths.

In the cases of uniaxial crystals it will be clear that the singular axis of tetragonal, hexagonal, or trigonal symmetry, which is also the axis of the optical velocity or optical indicatrix ellipsoid of revolution, must also be the axis of the absorption ellipsoid. In the case of a rhombic crystal, the absorption axes are identical with the three rectangular axes of the optical ellipsoid, which are also the three crystallographic axes a, b, c. In the case of a monoclinic crystal the axis of symmetry, the crystallographic axis b, is bound to be identical with one of the absorption axes, but the other two axes of the absorption ellipsoid, while bound to lie in the symmetry plane like the two other axes of the ordinary optical ellipsoid, may lie anywhere at right angles to each other in that plane, and in general are not identical in direction with the two axes of the optical ellipsoid. In the case of a triclinic crystal, none of the axes of the absorption ellipsoid are, in general, identical with the axes of the optical velocity ellipsoid or indicatrix, or with any of the crystallographic axes a, b, c.

The mathematical conditions for these absorption ellipsoids have been worked out for the different systems by W. Voigt [1] and P. Drude,[2] and the latter has shown that in biaxial crystals there are two axes of equal absorption, equivalent to but in general not identical with the optic axes as regards direction, although in the rhombic system they also like

[1] *Wied. Ann. der Physik*, 1884, *23*, 577.
[2] *Wied. Ann. der Physik*, 1887, *32*, 584, and 1890, *40*, 665.

the latter lie in one of the three symmetry planes, and in the monoclinic system either lie in the symmetry plane or in one perpendicular thereto.

It will have been gathered from what has already been stated that two kinds of crystals are to be distinguished as regards absorption of light, namely, those which are only slightly absorptive, and therefore more or less transparent, and those which are strongly absorptive. The ordinary laws of reflection, transmission, and refraction apply to a large extent to the former; but the latter exhibit remarkable and often uniquely distinctive properties, especially that of surface coloration, sheen, and metallic lustre, accompanied by more or less opacity, which will be dealt with later in this chapter.

Before further developing this subject of the absorption of light in crystals, however, a simple means of investigating it will be described.

Pleochroism or Dichroism, as it is variously called, may be quite well investigated under the microscope, using a single Nicol. Or it may be examined in a manner which places both colours side by side in the same field of view, by means of the little instrument devised by Haidinger and known as a "dichroscope," shown diagrammatically in Fig. 810. The dichroscope is essentially a simple form of double-image prism of Iceland spar. A single rhomb of the spar S fills the greater part of the optical tube T, which has a large round aperture at the eye end E and a small square aperture A at the other end, against which the crystal C is to be held. The oblique ends of the rhomb are squared with prisms of glass G, and immediately in front of the near one is placed a plano-convex lens L, calculated to focus the square aperture when the rhomb is removed. When the latter, however, is in position two images of the aperture are afforded, and the length of rhomb and size of square aperture are so chosen as just completely to separate them. The conditions are shown in Fig. 811, the shaded square marked ω occupying a central position in the field, being that due to the ordinary rays, while the other, labelled ϵ, represents the image due to the extraordinary rays. When the crystal plate is introduced behind the rhomb, with the extinction directions parallel to the longer and shorter diagonals of the rhomb, ω shows a colour due to rays which have vibrated in the crystal and in the rhomb in the direction parallel to the longer diagonal of the rhomb, and perpendicular to the optic

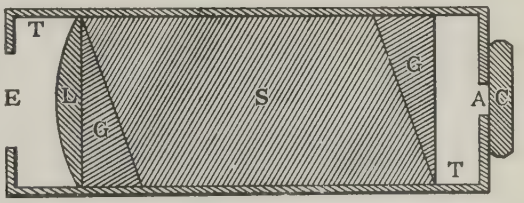


FIG. 810.—Section through the Dichroscope.

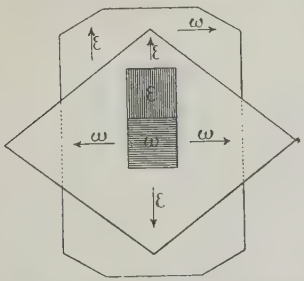


FIG. 811.—The Conditions obtaining in the Dichroscope when the Vibration Planes of the Calcite Rhomb and the Crystal are parallel.

axis and to the principal section containing the optic axis, while ϵ exhibits the colours imparted to the rays which have vibrated in the crystal and rhomb parallel to the shorter diagonal of the calcite, which lies in the principal section containing the optic axis. The colour of each square is the residual effect left after light of certain wave-lengths has been absorbed within the crystal from the original white light. On rotation of the crystal-plate in its own plane and about the axis of the dichroscope, the tints approach similarity, until at the 45°-positions they are the same; further rotation again invokes a difference, which becomes a maximum when 90° of rotation have been effected, the colours of the squares being now interchanged compared with those displayed at first for the 0°-position. The maximum difference of colour is thus always shown when the vibration directions of the crystal and the rhomb are parallel. It is an advantage to see in this manner side by side the two colours produced at their maximum difference, for very small degrees of dichroism can then be detected which would not perhaps be recognised with the polarising microscope.

Further Facts concerning Absorption.—In the case of a uniaxial crystal, a plate cut perpendicular to the axis, which thus transmits rays parallel to the axis and vibrating perpendicularly in all azimuths thereto, always shows the two halves of the dichroscope field equally illuminated and tinted, as the absorption is equal and similar in all directions perpendicular to the axis, including therefore those parallel to the two vibration directions of the calcite rhomb of the instrument. The maximum absorption occurs either parallel to the axis, and the minimum absorption perpendicular thereto, or *vice versa*. It generally happens that a rule first observed by Babinet is followed, namely, that the more highly refracted ray (the ordinary or the extraordinary) is absorbed more considerably than the other less highly refracted one. So that in the case of positive crystals the extraordinary ray is the more absorbed, and in negative crystals the ordinary ray.

The variety of *chlorite* known as **Pennine** is an excellent example of a very strongly pleochroic uniaxial crystal. It is a hydrated silicate of alumina and magnesia, $Si_8Al_4Mg_{13}H_{20}O_{45}$, forming, as found at Zermatt, large dark green crystals belonging to the ditrigonal scalenohedral class 21 (calcite class) of the trigonal system. They are usually hexagonal plates with the edges bevelled by faces inclined $66\frac{1}{2}°$ to the basal plane. The basal cleavage is perfect, and cleavage plates, which are thus perpendicular to the axis, appear emerald green, while plates cut parallel to the axis appear brownish red. When one of the latter plates is examined in the dichroscope the colour in the patch formed by light vibrating perpendicularly to the axis (parallel to the cleavage trace) is bright emerald green; while the other patch, formed by light vibrating parallel to the axis (at right angles to the cleavage cracks) is coloured yellowish brown or reddish. Thus a single plate of a uniaxial crystal suffices to determine the nature of the absorption, with the aid of the dichroscope, or even of a single Nicol, or any other means of determining that the incident light shall have a known direction of vibration.

Some crystals of chlorite, doubtless owing to isomorphous replacement of the magnesia by other heavier oxides, afford cleavage flakes exhibiting slightly biaxial characters, with a small optic axial angle; and in all cases the double refraction is very feeble indeed, the two refractive indices of pennine being nearly identical, $\omega = 1{\cdot}577$ and $\epsilon = 1{\cdot}576$, and corresponding to negative sign. So close are these values that they are sometimes inverted, the crystals being of feeble positive double refraction. While thus the typical pennine variety of chlorite appears to be uniaxial, other varieties, as just mentioned, have been considered as monoclinic, but with strong pseudo-hexagonal (trigonal) character. Indeed, it has been suggested that chlorite may be built up of excessively thin biaxial lamellæ parallel to the form {111}.

Another excellent example of strong pleochroism, and one which is unquestionably truly uniaxial, is **magnesium platinocyanide,** $Mg\,Pt(CN)_4 . 7H_2O$. This beautiful salt consists of red tetragonal prisms, which exhibit a greenish sheen about the middle exterior parts of the prisms and a blue sheen near the terminations.[1] When a plate is ground perpendicular to the tetragonal axis, or a natural cleavage plate is taken (the prisms cleaving readily perpendicularly to the axis), and held up to the sky, preferably with a white cloud as background, one sees, on approaching the eye fairly closely, a round violet spot on a vermilion ground. The explanation is afforded by the fact that the colour of the light transmitted by the crystals is carmine red of different shades according to the direction, the shade of the light produced by vibrations perpendicular to the axis being more bluish, while that of the light vibrating parallel to the axis has less blue with the red. These facts can be confirmed by examining a plate ground parallel to the axis, in the dichroscope, the two patches of light vibrating respectively parallel and perpendicular to the axis being red and violet. If the plate perpendicular to the axis be very thin blue predominates in the tint observed, but if the plate be thick practically only red is observed. With a suitable medium thickness of plate perpendicular to the axis, the colour is violet, a mixture of red and blue, near the centre of the plate, but passes into red at the edges, as the inclination to the axis increases.

A biaxial crystal is at once distinguished from a uniaxial one, as there is no orientation of plate-cutting for which two equally and similarly coloured patches are observed on rotating the plate in the dichroscope. In order to determine the character of the absorption along all three axial directions of the optical and absorption ellipsoid only two plates are necessary, cut so as to be perpendicular to two of those axes. A plate cut perpendicular to one of the three axes of the ellipsoid, say the α axis of the indicatrix, will afford in the two respective patches of the field of the dichroscope, when the two axial directions β and γ lying in the plane of the plate coincide with the two vibration directions of the calcite, the two colours and intensities of the light vibrating along those

[1] Other platinocyanides also exhibit beautifully coloured "metallic" lustre or surface sheen, details of which are given on pages 1132 (potassium, ammonium, and barium platinocyanides) and 1120 (yttrium platinocyanide).

β and γ directions respectively. Similarly, a second plate perpendicular to either β or γ, say γ, will afford the intensities and colours corresponding to the two other directions, in the case chosen α and β. The two plates thus afford all three axial colours, that is, the colours of the light waves vibrating parallel to the three respective axial directions of the optical and absorption ellipsoid ; and in the case of one of the three the colour is afforded in duplicate. Indeed, the absorption phenomena of biaxial crystals are often referred to under the term " Trichroism," corresponding to the triaxial nature of the ellipsoidal surface of absorption.

Three of the most strongly pleochroic biaxial substances are cordierite (often called dichroite), epidote, and glaucophane.

Cordierite, $(MgFe)_4Al_4Si_5O_{18}$, the crystals of which are orthorhombic, a typical one being represented in Fig. 812, is supposed to owe its colour to the solid solution of a minute quantity of a foreign substance. When only vibrations parallel to the minimum axis a of the optical indicatrix, the vertical axis c of the crystal, are permitted to be transmitted the colour is bright yellow to yellowish brown. When the light is vibrating parallel to the intermediate axis β of the indicatrix, the brachydiagonal crystal-axis a, it appears bright blue or greyish blue. And when the issuing light is vibrating parallel to the maximum axis γ of the indicatrix, the macrodiagonal crystal-axis b, it appears dark blue. These facts will be clear from Fig. 812. Hence, when a plate of cordierite is cut parallel to the basal plane c (001), and viewed through the dichroscope, the two extinction directions of the plate being arranged parallel to the vibration planes of the calcite rhomb of the instrument (the longer and shorter diagonals), the two squares are seen to be coloured greyish blue and dark blue respectively. If the plate be cut parallel to the brachypinakoid b (010) the squares appear greyish blue and yellow ; and if the plate be cut parallel to the macropinakoid a (100) the colours are dark blue and yellow. Each plate, therefore, or tabular crystal parallel to each of these three primary faces, is dichroic, and the whole crystal is trichroic, or, as it is more generally termed, pleochroic. By ordinary light, without Nicol or dichroscope to determine its direction of vibration, the colour transmitted by each of these plates is a blending of the two colours seen in the dichroscope, the result being called the " Face Colour."

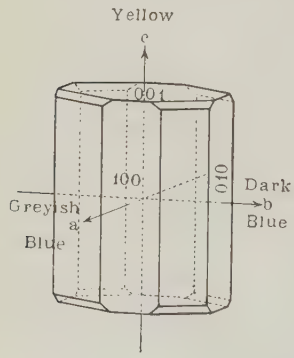


FIG. 812.—Crystal of Cordierite.

Epidote, $Ca_2Fe_2(FeOH)(SiO_4)_3$, this formula representing the beautiful ferruginous variety from the Sulzbachthal in the Tyrol, crystallises in monoclinic prisms parallel to the symmetry axis. The crystals are often very rich in faces ; a typical specimen showing the more important forms is represented in Fig. 813. The crystals appear yellow, brown, and green, when the vibration direction of the transmitted light is respectively parallel to the α, β, and γ axes of the optical indicatrix. The obtuse

bisectrix of the optic axial angle, γ, is only 2° 46′ from being perpendicular to (100). Some further absorption phenomena exhibited by epidote will be referred to in the section, next but one, on Absorption Brushes.

Glaucophane, $NaAlSi_2O_6(FeMgCa)SiO_3$, affords the colours light greenish yellow, violet, and ultramarine blue, along the three axial directions of the ellipsoid, these being the colours of the light vibrating parallel to those respective directions. The mineral generally appears of a blue colour, and crystallises in the monoclinic system, like epidote. Just as the first and second median lines (the acute and obtuse bisectrices of the optic axial angle) lying in the symmetry plane are dispersed, so the absorption axes of both epidote and glaucophane are considerably dispersed for the different wave-lengths of light.

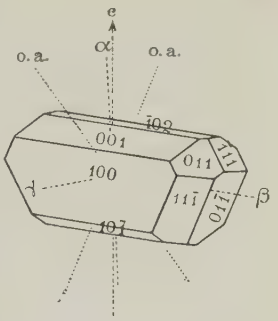


FIG. 813.—Crystal of Epidote.

The dichroism of the microscopic thin plates of crystals in rock sections is readily determined by employing a single Nicol, to fix the direction of vibration of the light which is being examined. The section is rotated, by rotation of the microscope stage, until the extinction positions 90° apart are located by use of both Nicols crossed; the colour of the light can then be observed for each of these same positions while one Nicol only is retained in position.

Absorption Brushes.—Transparent crystals of epidote exhibit a remarkable phenomenon, owing to the very strong absorptive properties of the mineral. When viewed through a (101) or (10$\bar{1}$) face in the direction of an optic axis (which is visible in convergent polarised light through a parallel pair of these faces), what are known as absorption brushes are seen, a pair of dark brushes of hyperbolic form directed towards a central light spot between them. They are due to the fact that for rays very near the optic axis the vibration direction of the light, and therefore the absorption, differs very greatly. **Andalusite** from Brazil also shows the phenomenon well, through a plate cut perpendicular to one of the two optic axes. With a plate of either of these minerals, held up to the sky and with the eye fairly close, one sees on a coloured ground of the natural colour of the plate the two dark hyperbolic brushes, as indicated in Fig. 814, with a bright diffused spot at the centre between them, and traces of a number of concentric rings.

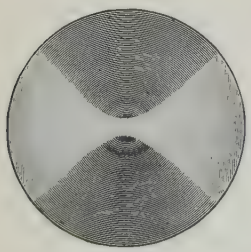


FIG. 814.—Absorption Brushes of Epidote or Andalusite.

A similar phenomenon of absorption brushes is also afforded by a plate, perpendicular to the axis (which, as already described on page 1117, may either be one prepared by cutting or a natural cleavage plate), of the uniaxial (tetragonal) very strongly absorptive and pleochroic substance magnesium platinocyanide, $MgPt(CN)_4 . 7H_2O$. In this case, however, it is necessary to interpose a Nicol between the eye and the

plate. It has been shown that the appearance without the Nicol consists of the exhibition of a violet colour in the central part of the plate, passing into a red colour in the marginal portion. With the Nicol, however, the violet disappears along the vibration direction of the Nicol, this ordinary colour of the plate, due to the admixture of the blue and red ingredients, being extinguished along that direction but permitted to pass along the direction at right angles. One sees, therefore, two red hyperbolic absorption brushes on a violet ground.

A curious and very beautiful case is that of the monoclinic tetrahydrated crystals of strontium nitrate, $Sr(NO_3)_2 . 4H_2O$ (not the better known cubic, tetrahedral pentagonal dodecahedral, class 28, anhydrous salt). When this hydrated salt, known as **"Senarmont's salt,"** from his early investigation of it, is crystallised at the temperature of 32° from an extract of logwood, it forms purple-red monoclinic crystals with strong red and dark violet pleochroism, the dye of the logwood having apparently entered into solid solution. A section-plate ground perpendicular to the first median line (12° inclined to the vertical axis, in the acute angle β of the crystal axes) affords two double absorption brushes.

Still more beautiful is the similar case of **yttrium platinocyanide,** $Y_2(CN)_{12}Pt_3 . 21H_2O$, which forms rhombic bipyramidal (holohedral) crystals of a bright cherry red colour and possessing strong pleochroism. A section-plate ground perpendicular to the first median line, the axis *c*, or a cleavage plate (the cleavage being parallel to *c* (001)), exhibits four hyperbolic absorption brushes, and the optic axial angle is so small ($2E = 27° 8'$, with very strong dispersion) that the four brushes appear as four red sectors, between which the ordinary colour of these basal plates shows itself as a violet cross. The absorption brushes are always perpendicular to the plane of the optic axes, *b* (010), and their middle points indicate the positions of the optic axes, so that this is a case in which the optic axes can be located without the use of a polariscope. According to Konig,[1] for light vibrating parallel to the vertical axis the crystals, especially when thin, are almost colourless, but for light vibrating perpendicularly to the vertical axis the crystal appears either bright red, golden yellow, bright green, or colourless, according to direction and circumstance, so remarkable are the absorption colour phenomena of this extraordinary substance. These facts, indeed, together with its external colour properties—for the basal plane, which usually largely predominates, appears bright crimson coloured, while the crystals exhibit a bright green surface colour on the prism and pyramid faces—justify the conclusion that this salt probably stands unique for its magnificent display of chromatic phenomena.

Radially arranged crystal-bundle aggregates, when pleochroic, also give rise to brush phenomena. A plate composed of numerous radially arranged uniaxial crystals, for instance, the length of the acicular crystals being parallel to the optic axis, affords the phenomenon. It may be imitated by causing a pleochroic crystal to rotate so rapidly as to produce the effect of a radial bundle. On regarding either the plate preparation

[1] *Wiedemann's Ann. d. Phys.*, 1883, *19*, 491.

or the single rotating crystal through a Nicol, or on placing the Nicol before the object, a cross is perceived, just as when two Nicols are employed as usual, but the two arms of the cross parallel to the vibration direction of the Nicol appear in the colour proper to the extraordinary ray, while the two other arms of the cross at right angles to the vibration direction of the Nicol exhibit the colour characteristic of the ordinary ray of the pleochroic uniaxial substance employed.

Surface Colours.—Ordinary white light reflected from most solids, whether they be coloured or not, is still white. But in a few exceptional cases it is more or less coloured. Some metals are well known cases, gold and copper for instance ; for a white object is reflected with a reddish colour from a polished copper plate, and with a yellow colour from a gold one. Other cases are crystals of non-metallic substances endowed with metallic lustre, and especially those reflecting a " sheen " or display of different colour from different faces. The platinocyanides of metals, and many of the aniline dye compounds, are examples of crystallised substances reflecting such remarkable varieties of surface colours or sheens. It is doubtless due to more or less penetration of the light rays within the crystal structure, and selective absorption there, while a portion of the light is transmitted, the substance being transparent to light of certain wave-lengths only. The surface colour is, indeed, complementary to the natural colour of the crystal, and as this natural colour, which is due to the transmitted light, varies with the direction in pleochroic crystals, the surface colour must also vary according to the direction of the light vibrations. In the case of a uniaxial crystal the surface colour is the same on all faces parallel to the axis, but different on faces inclined thereto, compared with the colour on the prism faces just referred to ; and the colours displayed by different individual faces of this inclined type may differ when the faces belong to different forms. The maximum difference of surface colour is in general that between the prismatic faces parallel to and the basal pinakoid faces perpendicular to the axis.

Magnesium platinocyanide, $MgPt(CN)_4 . 7H_2O$, tetragonal, is an excellent example concerning which it has already been shown that the natural faces or ground and polished surfaces parallel to the tetragonal axis exhibit by reflected light a green sheen or surface colour, and the basal plane a violet colour ; while the colour of the crystals by transmitted light is carmine-red for the extraordinary ray and violet-blue for the ordinary ray.

Thus these substances exhibiting surface colour appear to possess the power of preferentially selecting certain rays for reflection. A striking illustration is to dissolve a small quantity of one of the well-crystallising aniline dyes in alcohol and to pour a little out over a glass plate. On evaporation of the alcohol the thin film of the crystallised substance deposited on the plate appears one colour by the reflected light and quite another colour when the plate is held up and looked through. In the case of fuchsine, for instance, the appearance by transmitted light is rose-carmine, while it is bright green by reflected light. Moreover, a film of gold or of copper may be obtained sufficiently thin to transmit

some light, and this is of quite a different tint (dark red) to the surface reflection colour already alluded to.

Hence the light transmitted through such substances as exhibit surface colour reflection is deficient from two causes: first, by the loss from surface reflection, and, secondly, by loss in the interior of the crystal structure from absorption. As regards the light reflected, this consists of three portions, one of which is reflected under the ordinary law of reflection and is plane-polarised more or less according as the angle of incidence approaches that for maximum polarisation; it is accompanied by the second, which Preston terms an abnormal portion, that which has been selectively refused admission by the particular crystallised substance showing surface colour from which it is reflected. This portion appears not to be plane-polarised according to Drude,[1] but to a considerable extent, although not completely, polarised elliptically. The third portion of light turned back from entering the substance to any considerable distance is that which is scattered in the ordinary manner, by the inequalities of the surface, and by reason of which the eye really perceives the object; this part has just penetrated far enough to be affected by the selective absorption of the substance. This third portion is greatly reduced by giving the plate surface a high degree of polish, or using a freshly prepared cleavage plate. It is the mixture of all these three varieties of reflected light which produces the actual tint observed, the surface colour. This colour will change when a Nicol is interpolated between the object and the eye, largely by reason of the extinction of the true surface reflection, and by the effect of direction of vibration on the scattered portion which has also suffered some selective absorption. The elliptical polarisation of the abnormal selectively refused portion must, if it occur, have also its due effect as the Nicol is rotated. It is most marked with very strongly absorptive substances, such as metals, and the mineral crystals exhibiting metallic lustre, such as galena and antimony glance. As example of such change on interposing a Nicol, the fuchsine dye already referred to as appearing rose-coloured by transmitted and green by reflected light appears bright peacock blue when examined through a Nicol.

It is interesting that when the surface colour of a uniaxial crystal is examined with the dichroscope, it is found that when the plate employed is one cut perpendicular to the axis the two squares appear similarly and equally coloured and illuminated; whereas if the plate be one cut parallel to the singular axis the two patches are differently coloured and illuminated. Hence this light, which has penetrated somewhat into the crystal structure, has been converted (except when the plate is exactly perpendicular to the axis) into two oppositely polarised and unequally absorbed rays, similarly to the transmitted portion. This phenomenon, of course, is superposed on the ordinary surface reflection dealt with on page 805 of Chapter XXXVII., for which the reflection surface is responsible, and with regard to which polished glass serves as well as a crystal

[1] *Wied. Ann.*, 1887, *32*, 623; 1888, *34*, 489; 1890, *39*, 537. See also F. Pockels, *Lehrbuch der Krystalloplik*, 1906, p. 430-435.

surface. This additional phenomenon has to do essentially with light waves which have to a greater or lesser extent penetrated inside the crystal structure and been influenced thereby.

Drude (*loc. cit.*) has investigated several strongly absorptive metals from this point of view, including some which crystallise in doubly refractive crystal systems as well as those crystallising in the cubic isotropic system. He has determined their refractive indices and absorption coefficients from their surface reflection, as prisms and plates are not sufficiently transparent for direct refraction determinations. Very high refractive indices were obtained for the cubic-crystallising metals—lead, platinum, and iron.

In addition he has studied two minerals possessing in a high degree the so-called "metallic lustre," and it is interesting that the highest refractive indices yet known were found to be afforded by these two compounds, the cubic galena, sulphide of lead, PbS, and the optically biaxial (rhombic holohedral) antimony glance, stibnite, Sb_2S_3. For this latter substance, which is of more interest as being the only case fully investigated of a non-isotropic substance showing strong "metallic" absorption, the two refractive indices investigated each exhibited a maximum in the green near F and a minimum near the red end of the spectrum, the actual values of the two maxima being 5·53 and 4·52, the double refraction being thus 1·01. Both the absolute values of the refractive indices and the strength of the double refraction are the highest values yet obtained for these constants for any known substances. The observations were much facilitated by the fact that it is easy to obtain freshly cleaved plates of the substance parallel to (010). The refractive index of the isotropic galena was found for sodium light to be 4·30, employing a very perfect natural-cleavage face. As illustrating the effect of surface perfection, another crystal artificially polished afforded only the value 2·96. Combined with these high indices very low absorptive power was found. The cubic metals proved to have the following refractive indices: iron 2·36, platinum 2·06, lead 2·01, nickel 1·79, copper 0·64, gold 0·37, and silver 0·18. It will be observed that very low refractive indices were obtained for cubic silver and gold, in fact so low as to be less than unity, namely, 0·18 to 0·37. That means that the velocity of light vibration in these two noble metals is actually greater than it is in vacuous space. Together with this low refractive index, however, these metals also possess enormous absorptive power. This interesting fact has been since confirmed by Kundt, from experiments with thin films of the metals; the films were so excessively thin that he was enabled to work directly with the transmitted light, and thus to study the complementary phenomena to that experimented with by Drude.

Determination of Absorption of Light by Crystals.—The determination of the absorption coefficient, and the quantitative proof of its dependence on the direction of transmission or vibration of the light rays, the qualitative proof of which is afforded by the dichroscope, requires an apparatus which combines a spectroscope with a photometer for comparing the intensities of the two light patches. The two beams are separated by

double refraction as in the dichroscope, and are composed of light polarised at right angles; they are also arranged to be of equal intensity. The introduction of the absorbent crystal-plate then disturbs the equality of intensity, which is, however, restored again by rotation, for the necessary amount, of a Nicol polariser or analyser. There are two types of apparatus, of which the spectrophotometer of Glan and the microphotometer of Königsberger are characteristic examples which will be now described.

Spectrophotometer of Glan.—Any efficient spectrometer will serve as the basis of this instrument, and the one shown in Fig. 815 is the Fuess No. 2*a* goniometer,

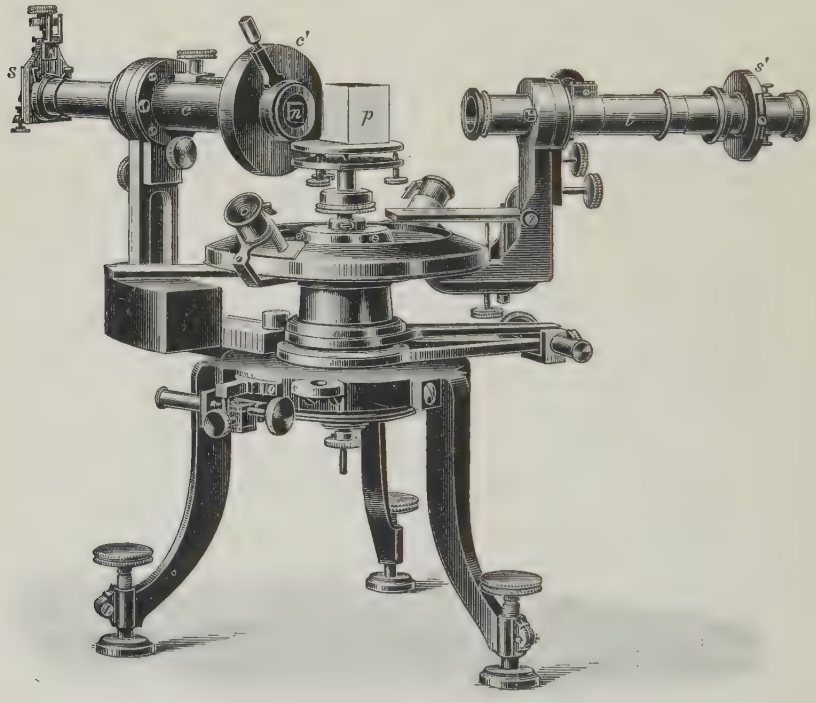


FIG. 815.—The Glan Spectrophotometer.

suitably modified for the special object in view. In this, and the succeeding sectional figure 816, *c* is the collimator, *p* the 60°-prism, and *t* the telescope.

In front of the objective of the collimator *c* a double-image prism *r* is mounted. It may be either of the Rochon type, which is in some ways preferable, and which gives an extraordinary image rotating about the ordinary one, or of the Wollaston type, which gives double the separation of the two sets of rays and furnishes two images rotating about a common centre, as fully described in Chapter XL. page 856. This double-image prism *r* is followed by a Nicol prism *n* provided with a large rotating circle *c'*. The slit *s* of the collimator, shown enlarged in the inset of Fig. 816 in order the more clearly to elucidate these essential details, is divided into an upper and a lower half by an opaque bar, and thus appears as two rectangular strips, A and B in

Fig. 817, when the double-image prism is removed. Each half is doubled, however, by the double-image prism when the latter is in position, the two images of each pair being rectangularly polarised and arranged to be above each other, as indicated in Fig. 817 at A_ϵ, A_ω, and B_ϵ, B_ω, the ordinary ray image A_ω of A being brought next to the extraordinary image B_ϵ of B. These four images are broadened out by the dispersion of the 60°-prism into four spectra almost in contact one above the other, as seen through the telescope *t*. The two outer ones are screened off by an iris diaphragm, so that only the two middle ones, corresponding to A_ω and B_ϵ, are visible. A second slit *s'*, devised by Vierordt, is placed at the common focal plane of the objective and eyepiece of the telescope, and this slit is adjustable for its position in the focal plane like a micrometer spider-line, and also for its opening. This enables the observer to select any part of the spectrum exclusively for examination at a time. The whole apparatus as constructed by Fuess is shown

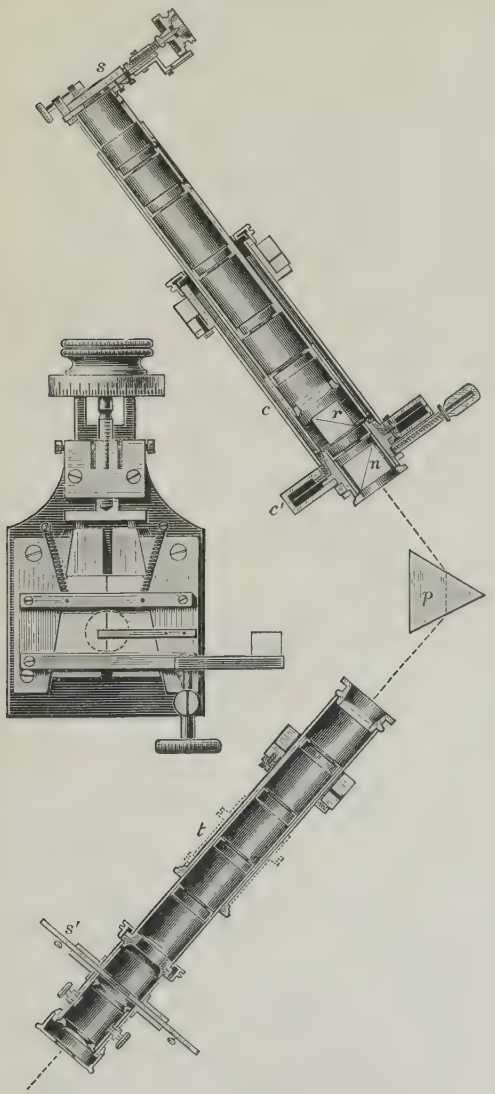


FIG. 816.—Section of Glan Spectrophotometer, and Enlarged View of the Slit.

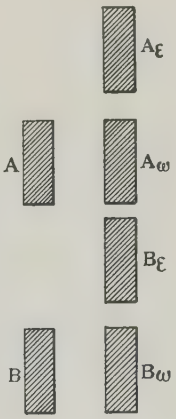


FIG. 817.

in Fig. 815, and a section through the optical tubes and prism, with an enlarged inset of the first slit, in Fig. 816.

In using the instrument the zero is first found by observing that position of the Nicol for which that one of the two spectra is extinguished, the vibrations of which are

parallel to the slit. The Nicol is then rotated for an angle α to that position for which the two spectra are of equal intensity, this angle being usually in the neighbourhood of 45°. In order to determine the absorption of a crystal-plate, the latter is placed in front of one of the halves of the slit; it will then be found necessary, in order to restore the balance of intensity of the spectra, to rotate the Nicol for an angle β (counting from the zero). When the plate is one of a singly refractive crystal it may be arranged at any azimuth to the slit; but when a birefringent crystal is under investigation, it must be arranged so that one of its extinction directions is parallel to the slit, and the observations must subsequently be repeated with the other extinction direction similarly adjusted.

If A_A and A_B are the coefficients of reduction of intensity by passage of the two sets of rays through the apparatus, coefficients depending on the apparatus itself and determined experimentally, and if I_A and I_B are the two actually observed intensities, then :

$$A_A \sin^2 \alpha = A_B \cos^2 \alpha, \text{ or } \frac{A_B}{A_A} = \tan^2 \alpha,$$

and

$$I_A A_A \sin^2 \beta = I_B A_B \cos^2 \beta,$$

when the Vierordt slit is used to compare equal portions of the two spectra. Hence,

$$\frac{I_A}{I_B} = \frac{A_B}{A_A} \cot^2 \beta, \text{ or } \frac{I_A}{I_B} = \tan^2 \alpha \cot^2 \beta.$$

This latter equation thus at once gives the ratio of the two intensities, from the data of the two observed angles α and β.

Königsberger's Microphotometer, shown in Fig. 818, is essentially a low-power polarising microscope in which the polarising Nicol prism is replaced by a double-image prism of calcite *a*, or a simple rhomb of adequate thickness of the mineral to afford the required separation of the images of two apertures employed.

Behind the double-image prism or rhomb is a diaphragm pierced by the two rectangular apertures. Four images of the latter are thus produced, and are so disposed, by suitable adjustment of the size of aperture and its distance from the double-image prism, that the extraordinary image of one aperture is partially superposed over the ordinary image of the other opening, the other two outer images being screened off by an iris diaphragm in the optical tube. The latter has an objective *b* of $3\frac{1}{2}$ inches (9 cm.) focus, an eyepiece *c*, and a fixed Nicol *d*. It is mounted in an adjustable manner which permits of its arrangement truly perpendicular to the calcite double-image prism. Either before or behind the objective comes a double quartz plate *e*, showing Savart's bands in feebly convergent light. A quartz plate cut parallel to the axis shows in convergent polarised light at 45° to the vibration planes of the Nicols, a series of hyperbolic curves, alternately dark and bright in monochromatic light but spectrum-coloured in white light, which have been illustrated in Fig. 699 (page 931) and which become narrower and sharper the thicker the plate; but beyond a certain thickness the coloured hyperbolæ in white light become fainter, and finally disappear for a very thick plate. The Nicols may be either crossed or parallel, the dark hyperbolic bands merely exchanging places with the bright interspaces. Two such plates superposed with their axes arranged perpendicularly afford more strongly coloured hyperbolæ in white light. When a plate of quartz is cut, however, at 45° to the axis the curves become approximately straight lines, and two such plates arranged with their principal section planes perpendicular to each other give straight lines, coloured in white light, but dark in monochromatic light, which bisect the angle between the principal sections. These are known as "Savart's bands," and have been illustrated in Fig. 701 (page 931). Such a compound quartz-plate acts as a very delicate test for the presence of polarisation, however feeble. It is quite adequate, in fact, to detect the polarisation of the light of the sky. The two plates of which the compound plate is composed should be the two halves of one and the same plate originally prepared, in order to

secure identical thickness of the two crossed plates. The sensibility of Savart's bands increases, moreover, as the plane of polarisation of the incident light, that of a polarising Nicol, for instance, in front of which the compound plate is held, approaches the bisector of the angle between the principal sections of the two plates, that is, the direction of the bands themselves. The Savart's bands disappear when the two superposed images of Königsberger's microphotometer, composed of ordinary and extraordinary rays respectively, vibrating perpendicularly to each other, are of absolutely equal intensity. Hence, to begin with, the light from the two orifices is equalised so that the bands are invisible. The moment one aperture is covered with the crystal-plate under investigation, which deranges the equality, the bands reappear. The absorption by the crystal is determined by the amount of weakening required by the light proceeding from the other aperture, in order to cause the bands to disappear again, and which is effected by means of a rotating Nicol prism *f*, provided with a

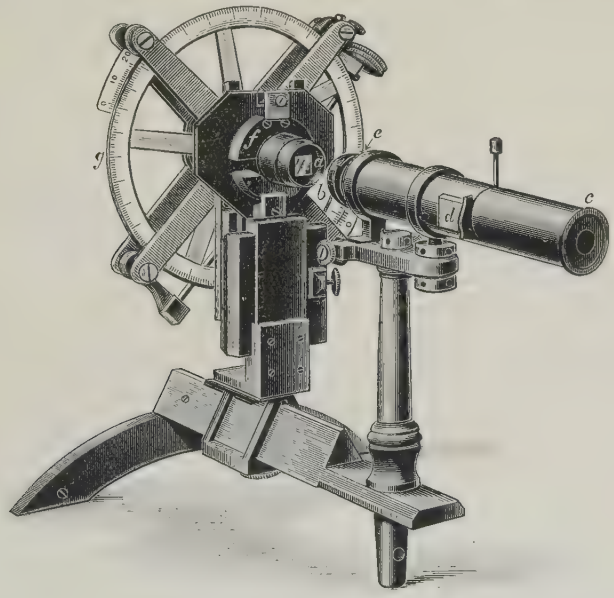


FIG. 818.—Königsberger's Microphotometer.

large divided circle *g*, which is operated as in Glan's photometer. Monochromatic light is required for the observations, which is furnished very satisfactorily by the spectroscopic monochromatic illuminator described in Chapter XLIV.

Pleochroic Haloes.—The examination of certain pleochroic and even some colourless minerals, especially under the microscope, has frequently revealed rounded spots of deeper colour than that of the mineral crystal in which they appear, and always more strongly pleochroic. The spots usually surround a microscopic inclusion. Such "pleochroic haloes," as they have been termed, were first observed by H. Rosenbusch in cordierite, andalusite, mica, and diopside. They were subsequently observed by Michel Levy, Traube, Cohen, and others, in biotite mica, tourmaline, and augite. It was further observed by Michel Levy that they were associated with certain specific mineral, inclusions particularly with zircon

in mica, allanite (a silicate of the epidote group) in the biotite variety of mica, dumortierite ($Al_8Si_3O_{18}$) in cordierite, and also with apatite, rutile, and cassiterite in the state of microscopic inclusion in other minerals.

These pleochroic haloes have given rise to much fruitless speculation. They were for long considered to be of organic origin, due to the local concentration of carbonaceous pigment, as it was found that heat often dissipated them to a large extent, the supposition being that the carbon became oxidised. This was not general, however, as others could only be removed by prolonged treatment with hydrochloric acid. It was then assumed that they were due to oxide of iron. The optical properties of that portion of the containing crystal which they occupy are altered by the presence of the halo ; in a cordierite examined by Wülfing, for instance, a change of one-tenth was observed in the double refraction.

With the discovery of the phenomenon of radio-activity, however, light has been thrown on this interesting subject of pleochroic haloes, and there is no longer any doubt that they are due to the ionising effect of the disintegration products of the radio-active elements thorium, radium, and uranium, and their isotopes or emanations (see Chapter XXXV.). The subject has been investigated in detail by J. Joly,[1] who has examined various micas from the Vosges, County Carlow, Ireland, and other localities, haloes of all types and in all stages of development having been found in them. The County Carlow micas were frequently found to be " dusted " over with black nuclear spots surrounded by haloes, the delicate rings interlacing and overlapping in all directions. Fig. 819 is a reproduction of drawings by Joly, retaining his numbering of the separate haloes, and shows the appearance of a number of these haloes under the microscope, the magnification being about 480 diameters. Fig. 1 (Joly's numbering) represents the first stage of a uranium halo, and Fig. 2 the second stage, showing rings 1, 2, 3, and 4. Figs. 3 and 4 show other uranium haloes in their third and fourth stages. Fig. 5 shows a uranium halo reversed by the action of heat. For it appears that those haloes which are not dissipated by heat are altered in this manner, which Joly terms reversal, and the process is akin to the well-known reversal effect met with in photography. Fig. 6 represents the first stage of a halo produced by the radium emanation. Figs. 7, 8, and 9 represent the first three stages in the development of a thorium halo. As a rule, the course of development is the same for both uranium and thorium haloes, but occasional differences are met with. They are almost always found to have been generated along a crack or vein. Their nucleus is in most cases zircon, and in others uraninite. This nucleus has the power of absorbing or occluding the emanation, and thus becomes a centre of radiation of the α-rays which accompany the emanation.

Pleochroic haloes are thus the result of the ionising effects of the α-rays (positively electrified helium-atom nuclei) proceeding from a central nucleus in which the radio-active substance, the emanation from radium, uranium, or thorium, is concentrated. The rays move along the radii of a sphere having the nucleus for its centre, diverging like rays of light

[1] *Phil. Trans.*, A, 1918, *217*, 51.

from a luminous point, and the effects diminish outwards inversely as the square of the distance. But as each particle experiences a rapid increase in

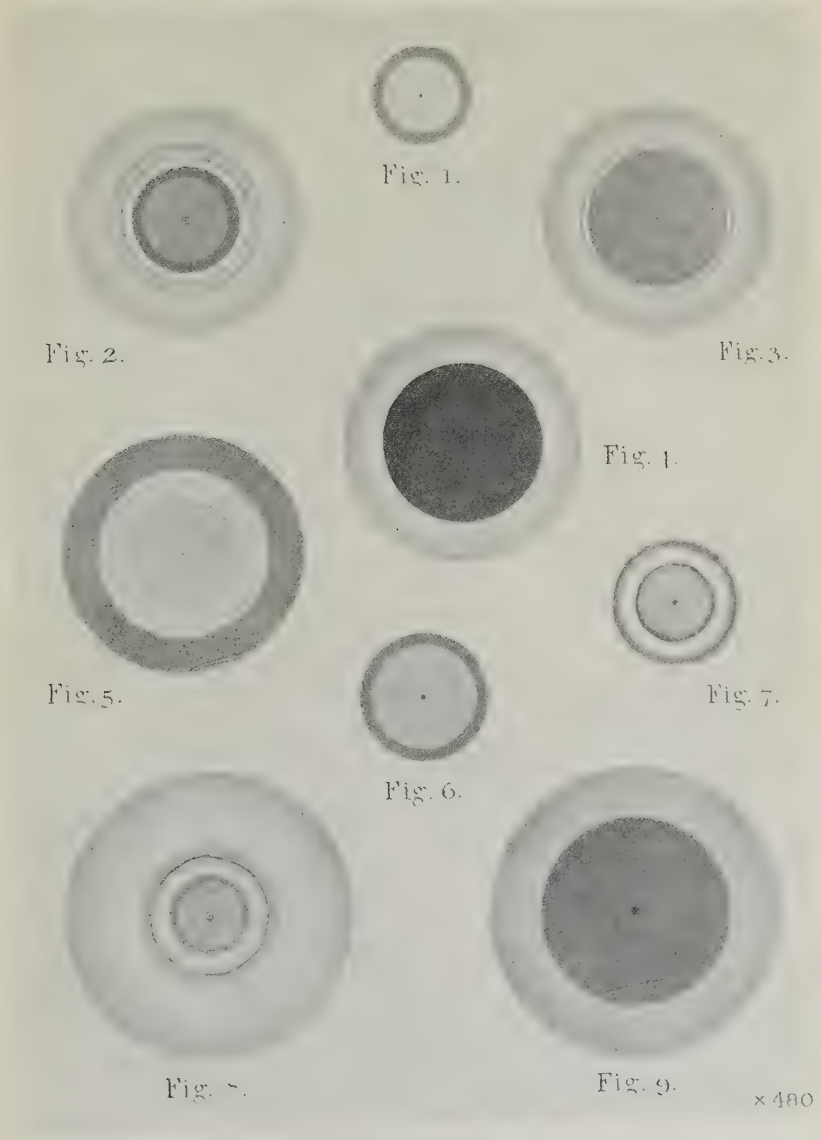


FIG. 819.—Pleochroic Haloes. Reproduced from Drawings by Prof. J. Joly.

its power of ionisation just before it loses its kinetic energy, in accordance with a law discovered by Sir William Bragg, the inverse square effect has this further effect due to the Bragg law imposed upon it. Hence, the

effect observed is not a simple one of gradual shading off, but one consisting in the development of a spherical shell of special action, the section being a ring, at a certain distance from the centre. The curve of energy, in fact, shows that several such shells may be produced, the section by the plate which cuts through them being a series of corresponding rings. For rock sections of ordinary thinness, and cleavage flakes of mica, include only a part of the total halo-sphere, perhaps one-third or a quarter of it.

Thus Joly concludes that the succession of shells, represented in section by concentric rings, represents the power or intensity of ionisation, the successive rings exhibiting different shades or densities of colour. In the first stage we have a delicate ring, which then becomes darker inside, forming a dark central pupil; then an outer ring is formed, the development of the shells and rings being just what would be expected from the curve of ionisation. The thorium haloes generally show at first two delicate concentric rings, the area within the inner one being more or less darkened; occasionally a third ring is formed, the radius of this outer ring being in one case, which was measured, 0·022 millimetres. The third stage often obliterates the inner rings and forms a deeply stained pupil. The extreme magnitude observed by Joly in the case of these haloes was a radius of 0·028 mm. The total result is the sum of the effects of all the α-rays concerned in the genesis of the halo. Every feature corresponds to the features of the integral curve of ionisation proper to the family of radio-active elements concerned, the relative spacing of the rings and their intensities being exactly paralleled by the features of the curve. The haloes agree, moreover, with the additive law of Bragg regarding the stopping power of mica, as determined for the same kind of mica as that in which the haloes were observed.

Although much more work requires still to be done concerning pleochroic haloes, there can be no doubt that Joly has arrived at a correct explanation. The nature of the chemical processes brought about in the ionisation, which give rise to the colours and darkenings, has still to be determined, and besides information concerning this aspect of the haloes it is probable that future research with them will throw additional light on the nature of radio-activity itself, and of the ages and approximate date of formation of the crystalline minerals in which they are found.

Luminescence.—Luminescence is the term applied to the phenomenon of light emitted by cold bodies, as distinguished from the ordinary light usually produced by raising the temperature of a body so as to effect either glowing without chemical action, or combustion with chemical action. Raising a solid to a temperature of about 400° C. usually causes dull red glowing, assuming no chemical action to occur; a white heat is produced about 1000° C., and the most brilliant artificial light, that of the electric arc between carbon poles, is produced at a temperature not exceeding 3500° C. The better known luminescent phenomena are those of fluorescence and phosphorescence, but many other forms are known, some of which are of crystallographic importance, and it will be best to consider them in consecutive order, with reference to their origin and nature, under group headings.

Chemical Luminescence.—An excellent example of the production of light at the ordinary temperature by slow chemical action is afforded by the case of phosphorus, slowly oxidising in moist air or oxygen, probably to phosphorous oxide P_4O_6 or (with the water vapour) phosphorous acid $P(OH)_3$, or of P_4O_6, further to phosphoric oxide P_4O_{10} or phosphoric acid. The glow is of a pale greenish-white character. The light emitted by the glow-worm, and by the fire-fly, as well as that given forth by marine organisms, by decaying fish, and decaying vegetable matter, especially fungi, is probably in all cases of chemical origin, and in most is connected with the presence of phosphorus in some form or other.

The phosphorescence of the sea is due largely to myriads of excessively minute *infusoria*, the chief of which is the *Noctiluca miliaris*. But many medusæ, star-fish, molluscs, nereidæ, crustaceans, and certain species of fishes, are also endowed with the ability to produce phosphorescence of the sea, and many of these creatures possess a controlling power, enabling them to emit the light or to shut it off at will. The source of the light in the case of medusæ, especially *Aurelia phosphorica*, appears to be a viscous liquid which was isolated by Spallanzani and found to contain phosphorus, which is also well-known to be a prominent constituent of fishes, phosphoretted hydrogen being the gas to which the intolerable odour of decaying fish is due.

Besides the occasional emission of light by decaying wood and vegetable matter, certain fungi and mycelia, one of which has been observed in dark cavities on Dartmoor,[1] also appear to possess the property of glowing in the dark during growth. The *Agaricus Gardneri* of Brazil gives out a light of a pale greenish tint, similar to that of fire-flies; and other species of *agaricus* in Australia are described as emitting a phosphorescent light strong enough to read by.

The phosphorescence of the element phosphorus is undoubtedly due to oxidation. From the garlic odour which accompanies the pale greenish-white light it is clear that P_4O_6 is concerned as a product of the oxidation occurring at the ordinary temperature, and the glow is due to the further oxidation of the vapour of this oxide to P_4O_{10}.[2] Ozone is also produced during this oxidation. The glow ceases in inert gases such as nitrogen or carbon dioxide, and in air it ceases if the air be compressed, or if ozone destroyers, such as turpentine vapour, be admitted. In oxygen the temperature requires to be at least 15°, unless the oxygen be diluted or its pressure reduced.

It has also been shown by H. Ebert and B. Hoffmann[3] that very carefully purified phosphoric oxide P_4O_{10} phosphoresces with a green light after strong illumination. This is quite distinct from the pale greenish-white chemical luminescence just referred to, due to the oxidation of P_4O_6 and possibly phosphorus itself in minute quantity. The green phosphorescence of P_4O_{10} becomes stronger as the temperature is reduced, until in a liquid-air bath at $-180°$ C. it affords a brilliant display of bright green light. It is noteworthy that this phosphorescence is given by the pure substance, for extraordinary precautions were taken to render the P_4O_{10} absolutely pure.

Phosphorescence and Fluorescence.—**Phosphorescence** is the luminosity of the kind exhibited by the various preparations of calcium, strontium, and barium sulphides, CaS, SrS, and BaS, such as Canton's "phosphorus," Balmain's luminous paint, and Bologna stone, a fibrous variety of barytes $BaSO_4$ reduced to BaS by heating with charcoal. An object coated with one of the luminous paints, after exposure for one minute to the light from an electric arc, will exhibit a brilliant blue phosphorescence for several minutes, and the luminosity is persistent in a lesser degree for many hours or even days and weeks. The most effective are the more actinic blue and violet rays, and especially the ultra-violet rays, the red end of the spectrum being ineffective. Hence, the curve of chemical actinism and photographic action is practically also

[1] This may be the *Polyporus annosus*, which has also been found phosphorescing in the Glamorganshire coal mines.

[2] See Thorpe and Tutton, *Journ. Chem. Soc.*, 1890, *57*. 545 for isolation and properties of P_4O_6 (oxidation 569).

[3] *Zeitschr. für phys. Chem.*, 1900, *34*, 80.

that for effective action in promoting phosphorescence. This important fact would appear to render it reasonable to suppose that chemical or physico-chemical action, or chemical molecular change, is again the cause of this phenomenon.

Red and orange light rays exert a destructive effect on phosphorescence, promptly extinguishing it. This remarkable fact was observed long ago by Goethe, and is referred to in his *Farbenlehre*.

The colour of the luminescence is characteristic of the particular substance, and independent of the colour of the exciting light, except that, as a rule (not absolute as formerly supposed), the emitted phosphorescent waves are longer and of lower refrangibility than the exciting ones. With the aid of the phosphoroscope of Becquerel, which enables the time period to be determined, it has been found that calcspar glows with an orange-coloured light for one-third of a second after exposure to greenish-blue F-light. According to Nichols [1] the property is due to calcium oxide impurity. A ruby emits a brilliant rose tint for one-twentieth of a second, and a sapphire behaves similarly, although not so brilliantly. The case of ruby is remarkable, for green light is converted into red phosphorescence, and the crystal itself is also red in the ordinary sense. Uranyl nitrate, $UO_2(NO_3)_2 . 6H_2O$, emits a green phosphorescence for the one-hundredth part of a second, after exposure to violet G-light. It is an interesting fact as regards uranyl nitrate, that Nichols and Merritt [2] have shown that the three different known hydrated salts with $6H_2O$, $3H_2O$, and $2H_2O$ afford quite different fluorescent spectra, the absorption bands being as different as if they were uranyl salts of three different acids. This indicates clearly that the water of crystallisation is a true part of the crystal structure. It also indicates that fluorescent spectra are due to vibrations which occur in the outer parts of the molecule. Diamond (some diamonds, not all) exhibits a blue phosphorescence for a very small fraction of a second, and the glow then changes its colour to yellow. The green variety of fluorspar, CaF_2, known as chlorophane, emits first blue light, then orange, and subsequently green light. The beautiful salts, the platinocyanides of barium, magnesium, potassium, and ammonium, shine for the minute time of about the one three-thousandth of a second, with a great variety of colour tints. The exquisite dichroic crystals of these salts of platinocyanhydric acid, $H_2Pt(CN)_4$, have the composition $BaPt(CN)_4 . 4H_2O$, $MgPt(CN)_4 . 7H_2O$, $K_2Pt(CN)_4 . 3H_2O$, and $(NH_4)_2Pt(CN)_4 . H_2O$. The barium salt consists of monoclinic prisms which appear green in the direction of the prism axis, and yellow with a bluish-violet sheen in directions at right angles to the prism axis. The magnesium salt consists of red tetragonal prisms with greenish sheen on the middle of the prism and blue near the terminations. The potassium salt forms yellow rhombic prisms, which appear blue along the direction of the prism axis. The ammonium salt forms white needles, but another ammonium salt is also occasionally obtained in yellow prisms containing $2H_2O$, which are also dichroic. The barium salt is the most readily prepared, hydrocyanic acid HCN being led through a solution of platinous chloride $PtCl_2$ in which barium carbonate $BaCO_3$ is suspended, as long as carbon dioxide is evolved, the solution being then set to crystallise. The magnesium salt is obtained by decomposing the solution of the barium salt with a solution of Epsom salts $MgSO_4 \cdot 7H_2O$.

The ordinary sulphide of strontium, SrS, phosphoresces persistently green however long it continues to phosphoresce. A second variety of this substance, however, quite distinct from the ordinary variety, phosphoresces violet, and if slowly warmed up to 200° gradually and continuously changes tint, being blue at 40°, green at 70°, yellow at 100°, and orange at 200° C., so that the colour is here dependent on the temperature.

Fluorescence is the name given by Sir George Stokes to the similar phenomenon which was exhibited by the " Blue John " variety of Derbyshire fluorspar, of emitting from its surface a green light during, and not after, its exposure to violet light or

[1] *Phys. Rev.*, 1918, *11*, 351.

[2] *Phys. Rev.*, 1917, *9*, 113.

ultra-violet rays. This non-persistent luminescence is also exhibited by uranium glass, quinine crystals, $C_{20}H_{24}N_2O_2$, the platinocyanides, eosin, and many other coal-tar products. It is also exhibited by many liquids, particularly by solutions of quinine (in dilute sulphuric acid H_2SO_4, nitric acid HNO_3, phosphoric acid H_3PO_4, or acetic acid $C_2H_4O_2$, but not in hydrochloric acid HCl), chlorophyll, and the beautiful substance fluorescein. The most remarkable characteristic of fluorescence is that it is best excited by ultra-violet rays,[1] invisible to the eye. These rays of very short wave-length and high refrangibility are thus instantaneously converted into visible light rays of longer wave-lengths and lower refrangibility. For instance, when such ultra-violet rays, or even the rays from the electric lantern filtered through several plates of deep violet glass, are passed through a dilute solution of quinine in either sulphuric, nitric, phosphoric, or acetic acid, the liquid glows with a magnificent blue fluorescence, and the incident beam has been deprived almost completely of its ultra-violet rays. Under the same circumstances (but in dilute alkali solution) fluorescein, $C_{20}H_{12}O_5$, an orange-coloured coal-tar dye, fluoresces with a brilliant green light. Its tetra-bromo derivative eosin, $C_{20}H_8Br_4O_5$, a scarlet dye, fluoresces with an orange light, and the more brilliantly when the solution is dilute. Chlorophyll, the green colouring-matter of the leaves of plants, fluoresces with a deep red colour.

Generally speaking, as already mentioned, both fluorescence and phosphorescence are excited by waves of higher refrangibility and shorter wave-length than those of the glow emitted. But it is not safe to assume this to be an absolute rule, for some dyes of high absorptive power fluoresce with a more refrangible light than that of the incident rays; for instance, naphthalene red emits a brilliant orange light when excited by light filtered through a ruby-red glass permitting only red and orange rays to pass, and spectroscopic examination of the orange fluorescence shows it to comprise both green and yellow rays as well as orange. Nichols and Merritt have shown that absorption and fluorescence are not related as a simple resonance, and that the position of maximum fluorescence is independent of the exciting light, so that the latter may even be on the red side of the fluorescent maximum. The fluorescence may be produced by any wave-length included in the absorption band, even if it happen to be longer than those emitted.

Thus the only distinction between fluorescence and phosphorescence is that the former is merely transient, occurring only so long as the exciting rays operate; whereas phosphorescence persists for a longer or shorter time after the exciting cause is removed. Fluorescence, however, occurs with many liquids, whereas purely physical phosphorescence is not known in the case of any liquids, the only phosphorescent liquids being those containing phosphorus, which are cases of chemical luminescence. Border-line cases are the platinocyanides of magnesium, barium, potassium, and ammonium, their brilliant phosphorescence occurring for so short a time, estimated as above stated at one three-thousandth of a second, after the shutting off of the exciting light. The beautiful case of fluorescent green uranium glass is that of a dilute solid solution of uranium glass in ordinary glass, for when the percentage of uranium is at all considerable, the glass being then a dark green, no fluorescence is observed.

It has indeed been stated that no pure substance phosphoresces, and that the phenomenon is essentially a property of diluted matter. Thus the late Sir William Crookes found that samaria (oxide of the rare element samarium) phosphoresced until by fractionation it was eventually got pure, when the glow suddenly ceased.

[1] A spectroscope provided with a complete quartz train of lenses and prisms is best used for work with violet and ultra-violet rays, as glass stops (absorbs) most of the ultra-violet rays, whereas quartz is singularly transparent to them. Such a train of quartz enables the fluorescent liquid to be tested in all the colours of the spectrum, and beyond it, and it is found with quinine that the maximum fluorescence occurs when the liquid is placed in the violet part, and that it is almost as brilliant just beyond the visible spectrum in the invisible ultra-violet.

On the other hand, it has been stated that pure specimens of the sulphides of zinc and magnesium have been observed to phosphoresce, although some doubts have been expressed as to the perfection of the purity of these samples. As it is the hexagonal variety of ZnS only which phosphoresces, this may be quite true. For the action of the violet light waves is probably to cause a small amount of conversion to the more stable cubic variety of ZnS, so that the case is still essentially one also of dilution. Moreover, it has been shown by MacDougall, Stewart, and Wright[1] that amorphous precipitated ZnS (action of ammonium sulphide on solution of a zinc salt) exhibits no phosphorescence, heat being necessary to produce this condition. Thus, ZnS produced by deflagration of molecular quantities of zinc and sulphur is phosphorescent, and the best product of all is precipitated ZnS which has subsequently been heated (best in hydrogen) to 650°-900° C. for 1½ hours (not more), this product being microcrystalline. Specimens prepared at 650° give a blue phosphorescence, and those prepared at higher temperatures give greens and yellows. While pure ZnS is truly phosphorescent, a small quantity, even a trace, of common salt or zinc chloride admixture increases the brightness. Phosphorescence of ZnS is thus a function of the crystalline structure, and of the hexagonal variety which occurs naturally as wurtzite; for it is well known that the hexagonal crystalline variety is produced by heating precipitated zinc sulphide in a current of hydrogen. The greater brightness of the phosphorescence of the microcrystalline form than that of larger crystals is probably merely due to the greater extent of surface exposed. But when ground to powder in a mortar the power of the phosphorescence is reduced, so that there is a lower as well as higher limit to the size of the crystals. The discovery already alluded to, that pure phosphoric oxide P_4O_{10} phosphoresces with a green light, affords further confirmation that, at any rate some, pure substances do phosphoresce.

Wiedemann has suggested that phosphorescence is more or less persistent chemical luminescence, a kind of partial electrolysis into ions which, however, do not remain separate but gradually recombine with emission of light. In support, the fact is quoted that all known phosphorescent substances are bad conductors of electricity. Dewar has shown, moreover, that at very low temperatures, such as that of liquid oxygen, many substances which are not luminescent at ordinary temperatures, such as paper, vegetable matter, ivory, etc., become persistently strongly luminescent. Ozone, moreover, when rushing into an exhausted receiver, becomes phosphorescent. Oxygen and sulphur dioxide, and many other gases to a less extent, phosphoresce brilliantly in vacuum tubes during the passage of the secondary electric discharge from a Ruhmkorff coil.

It is thus now generally agreed that fluorescence and phosphorescence are essentially the same, only differing in the relative velocity of absorption and emission. When the velocity of emission of energy is equal to or greater than that of the absorption of energy, fluorescence occurs; but if the velocity of the emission be slower than that of absorption phosphorescence takes place, that is, persistence of the emission occurs for an appreciable time after the exciting cause has been removed. In some cases the velocity of emission is very small and the absorbed energy remains stored up in the substance for a very long time. It may, however, be released by heating the substance, when it is given forth as thermoluminescence.

Thermoluminescence.—Two well-known minerals, the green variety of fluorspar, chlorophane, CaF_2, and scheelite, tungstate of calcium, $CaWO_4$ (bipyramidal tetragonal), and also a third substance, wurtzite, the hexagonal variety of sulphide of zinc, ZnS, shine in the dark when heated. The phenomenon is sometimes termed "calorescence." Natural crystals of wurtzite are rare, but artificially prepared ZnS generally takes this hexagonal form, and is used largely for phosphorescent work, and in the radium spinthariscope of Sir William Crookes (Fig. 593 on page 763), and generally for

[1] *Journ. Chem. Soc.*, 1917, *111*, 663.

radium screen phosphorescence. Excellent tabular and prismatic hexagonal crystals were obtained by Deville and Troost by sublimation of ZnS in hydrogen, and by other methods both the plates and the prisms have been obtained well developed by Hautefeuille, Mourlot, Forstner, Traube, Lorenz, and Sidot. The class to which the crystals belong is the dihexagonal pyramidal, class 26. Lorenz's crystals exhibited clear polar hemimorphism. Calorescence is well shown when a few fragments of any one of these minerals are thrown on a hot shovel in a dark room, the pieces glowing as brightly as glow-worms. In the case of fluorspar the light continues to be emitted for hours, provided the heating be maintained. But eventually, in all cases, the light dies away. It can be restored, however, by exposure to light, or to the electric brush or spark discharge, or to the cathode rays *in vacuo*; in the case of fluorspar exposure to X-rays also restores its calorescence.

Two remarkable and somewhat exceptional cases are arsenious oxide, As_4O_6, and quinine, $C_{20}H_{24}N_2O_2$. In the case of arsenious oxide, the thermoluminescence only occurs when the temperature is raised to a particular point, slightly below that of volatilisation, when a sudden brilliant flash is emitted. Quinine is remarkable in exhibiting a good display of luminescence on cooling, but none on heating.

The peculiar case of sulphide of strontium, SrS, studied by Becquerel, has already been mentioned. This substance affords an orange phosphorescence at 200° C., and as the temperature falls the colour passes through yellow, green, and blue until it is violet at the ordinary temperature, and deep violet at −20°.

Triboluminescence.—It has long been known that certain crystallised solids become luminous when subjected to friction. The best known are sugar (saccharose, cane sugar, $C_{12}H_{22}O_{11}$, monoclinic sphenoidal), uranyl nitrate $UO_2(NO_3)_2 . 6H_2O$, and some diamonds. One liquid, pentadecyl-paratolyl-ketone, has also been observed to exhibit the phenomenon, to which the name triboluminescence has been given. In the case of sugar it is well seen when the crystals are crushed in the dark, light being freely emitted. The green crystals (rhombic bipyramidal) of uranyl nitrate were shown by Herschel in 1899 to exhibit yellowish-green triboluminescence on active rubbing. It is curious that only certain specimens of the diamond, and by no means every diamond, become luminous when rubbed in the dark, a fact which was observed by Boyle. It would appear as if the original author of the story of Aladdin's Lamp in the *Arabian Nights' Entertainments* were aware of the phenomenon, as he ascribes to friction the power of calling forth the marvellous properties of the wonderful lamp.

Zinc sulphide, precipitated from a solution containing some sodium chloride and a salt of manganese, and afterwards heated to 650° C., in order to render it microcrystalline (hexagonal variety), shines with an orange tint when cold and exposed to a bright light in the ordinary manner for provoking phosphorescence. The blue phosphorescence of pure ZnS, or ZnS mixed with a little NaCl, is thus altered by the presence of the manganese to golden orange. This product containing manganese is also most strikingly triboluminescent.

Crystalloluminescence.—This name is given to the phenomenon of light emission displayed by certain substances on crystallising, from solution or the liquid state. Arsenious oxide, As_4O_6, is the best known example, when it crystallises in octahedra from a hot labile-supersaturated solution of 2-3 parts of the amorphous oxide in 12 parts boiling concentrated hydrochloric acid. Light is emitted, a flash followed by more or less continuous luminosity readily visible in a darkened room occurring as each crystal is formed. It is curious, however, that recrystallisation is unaccompanied by any such crystalloluminescence. Potassium sulphate from aqueous solution is another instance, and water when rapidly frozen has also been observed to display the phenomenon. Four interesting cases described in 1918 by Weiser[1] are those of the chlorides of sodium and potassium and the bromide and iodide of

[1] *Journ. Phys. Chem.*, 1918, *22*, 480.

potassium, when precipitated from aqueous solution by hydrochloric acid. The bromide and iodide of sodium do not exhibit the phenomenon. Rapid stirring increases the effect. The light from sodium chloride is bluish-white.

From a survey of the literature, and experiments with arsenic oxide and potassium sulphate, Weiser concludes that both crystalloluminescence and triboluminescence are caused by chemical action. In the case of the substances which show both phenomena the colour of the luminescence, and probably therefore the chemical reaction occurring, are identical. While a considerable number of substances show triboluminescence, a comparative few exhibit the property of crystalloluminescence, and they are chiefly simple inorganic substances. He considers that crystalloluminescence is due to the rapid reformation of molecules hitherto broken up by electrolytic dissociation, and that triboluminescence of the same substance is due to the rapid re-formation of molecules previously broken up by the violent disruption of the crystals during the rubbing friction. It appears to be a fact, moreover, that all crystalloluminescent substances exhibit also the property of triboluminescence; but the reverse is not true. Owing to the conditions of crystallisation a state of strain is often produced in crystals, a very notable example being the diamond (see page 1143 and Fig. 820). If outside force be applied to such crystals before the lapse of adequate time has resulted in the attainment of internal mechanical equilibrium, a particularly violent disruption of the crystal occurs, with molecular decomposition and the development of triboluminescence.

Lyoluminescence.—This is a complementary phenomenon to crystalloluminescence, observed by Wiedemann, which occurs when the subchlorides of sodium and lithium are dissolved in water. Chloride of sodium or lithium is placed in a vacuum tube and subjected to cathode rays, when chlorine is evolved and the substance becomes orange or bluish coloured. When this coloured product, which was considered by Wiedemann to be subchloride of the metal employed, is thrown into water light is emitted.

Electroluminescence.—An interesting link between frictional luminescence and electroluminescence is afforded by the case of mica. When a large tabular crystal of mica is split into sheets in the dark, or an ordinary sheet of mica is split into two thinner ones, flashes of light are emitted, and the sheets are found to be electrified.

Electroluminescence proper, however, is that which is stimulated by an electric discharge. The effluve from a highly electrified point, the brightly coloured light produced at the place on a solid where it is struck by a spark discharge, and the bright glow produced in the well-known Geissler vacuum tubes when the secondary discharge from a Ruhmkorff coil is passed through them, are all instances of the phenomenon. Practically all the phosphorescent and fluorescent substances referred to in the preceding sections become electroluminescent, under the influence of the electric discharge in the rarefied gases enclosed within a so-called vacuum tube. The colour of the light emitted by hexagonal zinc sulphide ZnS, for instance, is green or blue, according to the purity and perfection of the vacuum. The brilliant phenomena exhibited by Geissler tubes containing different gases under very much reduced pressure, including the famous Gassiot cascade display, are frequently referred to as cases of "effluvioluminescence." The phenomena afforded at the positive and negative poles respectively are considerably different, and the discharges from the negative or cathode in high *vacuo* are far more interesting than those from the positive pole or anode. Hittorf first observed the phenomena, but it is to Sir William Crookes that we owe their detailed study, and an account of his work, which eventually led to the discovery of the X-rays by Röntgen, has been given on pages 758 to 761. Working in very high *vacua* of about one-millionth of an atmosphere, the cathode discharges were found to be propagated in straight lines from the cathode plate, throwing shadows on the walls of the tube of any object placed in their path, and causing brilliant luminescence of the tube walls other than where the shadow is thrown; the glow is

coloured bright yellowish-green in the case of soda-glass tubes, and pale blue if lead glass be employed for the material of the tube. If a diamond, ruby, or sapphire be included within the tube in the path of the cathode rays the crystal shines out brilliantly with its own colour luminescence. Moreover, if a concave cathode plate be employed the rays may be focussed on any object, when the latter is raised so highly in temperature as usually to be fused, even platinum thus melting. The cathode rays can be deflected by a magnet, but they are stopped by the thinnest layer of a non-conductor such as a film of mica or glass. They possess a certain amount of penetrative power, however, through conducting substances.

We now know, as has been made clear on page 758 in the introductory chapter (XXXV.) to Part III., that the cathode rays consist of projected negative electrons, β-rays, and that as the secondary effect of their striking the inclined platinum anode (anticathode) plate or the glass-tube walls X-rays are generated and projected in all directions outside the tube, as glass is pervious to the exceedingly short waves of the X-rays. The effect of the cathode rays in stimulating electroluminescence is immense, no less than 140,000 times as great as that of sunlight, according to Wiedemann.

Some remarkable curiosities are observed in connection with the phenomenon. Heavy flint glass, consisting of borate or phosphate of lead, is photoluminescent, that is, excited by light-waves, but not cathodoluminescent; while ordinary lead glass, silicate of lead, is both, the photoluminosity being green and the cathodo-glow blue. Crown glass affords a green photoluminescence, but a greenish-yellow cathodoluminosity. Moreover, the cathodoluminescent rays from emeralds, sapphires, and jacinths are polarised, but not those from diamonds, tourmalines, or topazes.

X-ray Luminescence. — This is the luminosity displayed by substances when exposed to X-rays. Barium platinocyanide, $BaPt(CN)_4 . 4H_2O$, is the best example, and is the substance chiefly used on the screens employed in X-ray medical examinations. The excessively minute wave-lengths of X-ray vibrations enable them to pass freely through many substances—aluminium and flesh, for instance—but they are arrested by others to a greater or less extent, such as lead and bones. A shadow of the bones of the hand or other part of the human body is consequently thrown on the screen coated with barium platinocyanide, when the part of the body concerned is placed in the path of the X-rays and in front of the screen. The imperviousness of lead to X-rays is made valuable use of in protecting, by means of leaden screens, the bodies of X-ray operators from the severely injurious action of the rays. Instead of the screen of platinocyanide of barium a sensitised photographic film or plate is found to act admirably in affording a permanent record of the shadow; for on development in the ordinary photographic manner a negative of the shadow is obtained. So familiar are we now with these X-radiograms, as obtained in the hospitals, that more need not be said, except to remark in passing what a magnificent boon this advance in pure science has proved in the Great War, in enabling injuries to the bones, and the presence of rifle and machine-gun bullets, shrapnel, shell fragments, etc., in the bodies of wounded soldiers to be diagnosed and located with absolute precision, and thus to enable the surgeons in a vast majority of cases to operate rapidly with certainty of success and a minimum of shock to the system. The result has been the saving of innumerable valuable and heroic lives.

We now know—thanks to the fact that the space-lattice structure of the assemblages of atoms in crystals acts as a space-grating for X-rays, reflecting and diffracting them because of the similarity in order of dimensions of atoms and X-ray wave-lengths—that the X-rays are vibrations of very minute wave-length; indeed they form a continuation in the direction of attenuation, after a very considerable interval of as yet unknown types of vibration, of the ultra-violet vibrations just beyond the more refrangible end of the light spectrum which are so effective in provoking phosphorescence. Moreover, the actual wave-lengths of many specific, "monochro-

matic," X-radiations have been accurately determined by means of crystals of which the space-lattice structural dimensions have first been absolutely ascertained.

The card-screens covered with a layer of platinocyanide of barium or potassium used in X-ray medical examinations owe their use to the similar action which X-rays exert, in stimulating the luminescence of either of these beautiful salts, to that exerted by ultra-violet waves and violet light rays. The light emitted under X-ray stimulation by the barium salt, which is generally used, is pale yellow, and that given forth by the potassium salt is bluish. The colour is due to the particular metallic base present. For we are dealing in these cases with vibrations provoked in the metallic constituent atoms of the salts, another proof of the fact that the X-rays can directly affect the atoms, the dimensions of the exciting vibrations being of the same order as the size of the atoms. The X-rays are clearly vibrations derived by the impact of the negative electrons, projected as cathode rays, against the anticathode plate or the walls of the Crookes vacuum tube. The β-rays projected from radium are similar in nature to the cathode rays, consisting also of negative electrons; and the γ-rays, secondarily derived from them by their impact against solid matter, are similar to X-rays.

The fluorescence or phosphorescence exhibited by inorganic salts when subjected to bombardment by high-speed cathode rays is characterised by the emission of the series lines of the metal present, and the energy required to produce the effect in salts of the same metal increases with the heat of formation of the salt.

Calcium tungstate $CaWO_4$, the natural form of which is the tetragonal bipyramidal (class 12) mineral scheelite (see Fig. 166, page 203), is also now coming into use for X-ray screens. The characteristic X-radiation from silver and platinum has been found most effective with such screens. It has been shown by P. Roubertie and A. Nemirorsky [1] that the tungstates of the magnesium group, especially cadmium tungstate, also become brightly luminescent under the action of X-rays. Moreover, they are not deteriorated, like barium platinocyanide, by prolonged action of the X-rays, and the luminosity is white, affording very sharp radiograms.

The phosphorescence of the hexagonal variety of zinc sulphide ZnS can also be excited by X-rays. A luminous paint, comprising zinc sulphide, ZnS (presumably the hexagonal variety, artificially prepared or natural wurtzite), and about 0·2 to 0·3 milligram of radium *per* gramme of ZnS, has come into extensive use during the war for watches and compasses for night-flying, and for the dials of other instruments employed in connection with aircraft. The luminescence is due to the bombardment of the zinc sulphide by the α-rays emitted by the radium. The medium used to fix the preparation on the surface coated is also effective in so far protecting the zinc sulphide from the α-rays as to prolong its life considerably for phosphorescent purposes; so that the decay of luminosity which is usually observed occurs only one quarter as rapidly as when the preparation is used without medium, in which latter case the life is about 200 days.

Bombardment of certain minerals by the β- and γ-rays from radium produces remarkable coloration, as well as phosphorescent phenomena. Fluorspar is particularly strongly affected. Thus, a colourless fluorspar from Matlock in Derbyshire, after one day's exposure to fifty milligrams of radium, became deep blue coloured. This colour was permanent in the dark, but was discharged by sunshine or gentle heating, after which exposure to radium again effected the blue coloration. The colour stains the whole crystal and is not merely superficial, so is probably due to the γ-rays. It is supposed that they effect dissociation of minute foreign enclosures, and the subsequent fluorescence is due to the recombination of the products of dissociation. (See also section on Pleochroic Haloes, earlier in this chapter.)

Fluorescent screens of barium platinocyanide have been employed during the Great War for secret night signalling to an observation post. The post and the

[1] *Comptes rendus*, 1919, *169*, 233.

signalling station were each provided with a special form of telescope, which acted in the two respective cases as receiver and transmitter of the signals. Each optical instrument had an objective lens of three inches diameter and twelve inches focus, and an ordinary eyepiece. The transmitter was fitted at the common focus of eyepiece and objective with a specially constructed 6-volt electric lamp with coiled-up filament; and the receiver was fitted instead with the fluorescent screen of barium platinocyanide. The transmitting telescope was directed at the observation post with the aid of the eyepiece, which enabled the officer signalling to see the post; a relatively narrow beam of light issuing from the objective when the lamp was switched on was thus directed at the post.

For signalling by day the light was filtered at its exit from the telescope through a deep red glass screen, and by night through another combination glass screen which enabled only ultra-violet rays to pass, all visible light rays being cut out. It was found possible to see the red day signals through the receiving telescope in the ordinary way, the red beam not being prominent enough to attract the enemy's notice; and at night the totally invisible ultra-violet rays were received on the fluorescent screen in the receiving telescope, this screen lighting up most brilliantly when the signalling officer sent out the ultra-violet signal. The instrument was fully effective over a range of six miles.

A somewhat similar device involving the use of fluorescent barium platinocyanide was used for naval convoy work at night. The receiver consisted of the objective lens, the barium platinocyanide screen the full diameter of the telescope tube, and an eyepiece mounted on a metal strip across the end of the optical tube, so that the observer could see round it when the fluorescent spot appeared anywhere on the screen; he could then bring the spot to the centre by the adjustments provided for the telescope, and observe with the eyepiece. The transmitter was a Cooper-Hewitt mercury lamp, surrounded by a chimney of ultra-violet glass, which only transmits the light corresponding to the one mercury line of wave-length 0·0003660 mm., which is well outside the visible spectrum. Signals from this lamp can be picked up by the fluorescent screen of the receiver when the latter is as much as four miles away, and the device proved invaluable for enabling the ships of a convoy to be maintained in their proper stations with respect to one another at night, when steaming full speed with all lights out, without the least indication to any enemy prowling about in the neighbourhood.

It is a curious physiological fact that this ultra-violet lamp is visible to the eye at close quarters owing to fluorescence of the retina of the eye itself; and the field of vision appears filled with a haze known as "lavender fog," owing to fluorescence of the crystalline lens of the eye. The observer's teeth also fluoresce, unless they happen to be artificial, when they appear black.

Special Points concerning the Luminescence of Crystals.—The light emitted during the phosphorescence or fluorescence of isotropic crystals is not polarised, even although polarised light be employed to provoke the luminescence. In the case of doubly refractive crystals the luminosity is partially polarised, not, however, with respect to the plane of incidence but with respect to the crystal symmetry. Grailich first observed this fact is his study of the platinocyanides. Later, Maskelyne observed the fact also in his study of the phosphorescence of emerald, sapphire, and cassiterite excited by the cathode rays in a number of Crookes tubes, some of Sir William Crookes' original tubes having been employed. Not only does the intensity but also the colour vary with the direction, in accordance with the symmetry of the crystal. Hence, it is

quite correct to refer to pleochroic fluorescence. The phenomena are much complicated if the crystal be also an ordinarily dichroic one, and account has then to be taken of such original dichroism in observing and recording the fluorescent dichroism. In consequence of the difficulty of properly doing so, most of the researches on this branch of the subject have been carried out with non-dichroic substances. The chief of these investigations were those of Sohncke.[1] Some of the results are as follows :

Calcite, even in the cases of the clearest Iceland spar, was found to exhibit the orange or bright red fluorescence already referred to, and which would appear to be due to minute enclosures of calcium oxide. The greater bulk of the light was found to be composed of vibrations parallel to the optic axis, and when the exciting light was composed of such vibrations the maximum fluorescent effect was produced.

Apatite showed fluorescence which was composed predominatingly of vibrations perpendicular to the optic axis.

Beryl exhibited dichroic fluorescence, the vibrations parallel to the hexagonal axis being blue, and those perpendicular to the axis reddish violet. A few specimens, however, were found to exhibit the reverse colours. The intensity of the two components was not appreciably different and each was best provoked by exciting vibrations parallel to these same directions.

Phosgenite, $PbCO_3 + PbCl_2$, afforded an exceptional result. For incident vibrations parallel to the tetragonal axis provoked predominating fluorescent vibrations perpendicular to the axis, and *vice versa*. The fluorescent emission vibrating perpendicular to the axis was in this case the stronger one.

Topaz afforded fluorescent vibrations only in the plane of the optic axes, and the most intensive were parallel to the first median line, the acute bisectrix of the optic axial angle.

Aragonite yielded fluorescent vibrations which were feeblest parallel to the first median line, and strongest perpendicular to the optic axial plane. When polarised exciting light was employed, the maximum effect was produced when the vibrations were perpendicular to the optic axial plane of the crystal.

Cerussite, $PbCO_3$, rhombic holohedral, behaved analogously to phosgenite, the component of the fluorescence parallel to the exciting vibrations being the minimum and not the maximum as regards intensity.

Cane sugar, saccharose, behaved like aragonite.

A highly interesting series of observations have been made by Pocchettino [2] on the action of the cathode rays on different faces of a crystal. The cathodic fluorescence or phosphorescence is notably chiefly a surface action, and thus the character of the crystal face becomes of importance. In most cases the fluorescent light proved to be polarised, but by exception calcite, corundum, anglesite, orthoclase, tourmaline, and topaz emitted only non-polarised light. In the case of uniaxial crystals the light from the basal plane proved always to be unpolarised, while that

[1] *Wied. Ann.*, 1896, *58*, 417 ; *Ber. der Bayer. Akad., math.-phys. Kl.*, 1896, *26*, 1.
[2] *Rend. Accad. Lincei*, 1904, *13*, 301, and 1905, *14*, 220.

from the other faces was generally polarised ; in the cases of anatase, zircon, beryl, and wulfenite the direction of the vibrations was parallel to the axis, while it was perpendicular thereto in the cases of apatite, scheelite, and phosgenite. Curiously enough, the inclination of the crystal face to the bundle of cathode rays was immaterial.

Pocchettino also found that glass in a state of strain, such as exhibits the well-known polarisation phenomena, also exhibits polarised fluorescence vibrations under the influence of cathode rays. He further showed that the fluorescence of the platinocyanides in X-rays, and also in the radio-activity γ-rays from radium, is largely composed of polarised vibrations.

Lommel [1] had found as early as 1879 that in the case of magnesium platinocyanide, which it will be remembered crystallises in tetragonal prisms, that the colour emitted changed with the angle of vibration of the exciting light, relatively to the tetragonal axis of the crystal. Sunlight filtered through a screen of blue and violet glass plates, and directed on the basal plane perpendicular to the tetragonal axis, provoked a scarlet fluorescence, whatever were the vibration direction of the polarised incident light. If the light fell on a face parallel to the axis, however, a dichroic fluorescence was produced, which was orange-yellow or scarlet-red according as the exciting light was vibrating parallel or perpendicular to the axis of the crystal. The green surface colour of the crystals disappears in violet light. The same two colours of the dichroic fluorescence are naturally observed when, instead of polarising the incident light, the light issuing from the crystal is examined through a Nicol prism, the plane of vibration of which is first parallel to and afterwards perpendicular to the axis.

Voigt has suggested [2] a theory of fluorescence which explains the undoubted influence in many proved cases of small amounts of admixed impurities, or the presence of a second kind of molecule, and which is in accordance with the idea of dilution generally accepted as underlying the phenomenon. He imagines that the electronic vibrations which are occurring in fluorescence are caused by the conversion (Umwandlung) of one kind of molecule into another, and that one kind may be present in bulk while the other kind need only be present to an almost infinitesimal extent, admixed with and largely diluted by the other, as it were. An excellent example is that of hexagonal zinc sulphide, the phosphorescence of which is excited by the β-rays ejected by radium, this being a distinct phenomenon to the flash produced momentarily by the α-rays, helium atoms, without their two negative electrons, discharged from radium. According to Voigt direct proof has been obtained of the conversion of a small quantity of the sulphide into the ordinary cubic form of zinc blende, as a result of the action of these electronic β-rays.

J. Perrin [3] has shown that the expulsion of an electron from an atom is accompanied by fluorescence, and that the reintegration of the electron in the atom (its return to the atom) is accompanied by phosphorescence, and this latter is persistent in the case of solids, and is facilitated by

[1] *Wied. Ann.*, 1879, *8*, 634. [2] *Arch. Neerland*, 1901, p. 325.
[3] *Ann. de Physique*, 1918 [ix.], *10*, 133.

agencies such as heat which diminish the rigidity of the solid, becoming then thermoluminescence.

Fluorescence of Active Nitrogen.—A remarkable kind of fluorescence accompanied by a change of chemical properties of the element has been discovered and investigated by Prof. The Hon. R. J. Strutt[1] (now Lord Rayleigh) in the case of gaseous nitrogen. By the action of the electric discharge, from the secondary circuit of a Ruhmkorff coil with Leyden jar condenser, on nitrogen under very reduced pressure passing through a vacuum tube, the gas is rendered capable of reacting with hydrocarbons, mercury vapour, and other gaseous substances, and at the same time glows with a bright yellow luminescence for some time after its withdrawal from the Geissler tube. When the ordinary high tension discharge, unaided by a jar condenser, is passed through nitrogen at the usual low pressure of a vacuum tube, the latter exhibits first, nearest the cathode, the Crookes dark space; next comes the blue negative glow, gradually falling off to the Faraday dark space, after which there comes the red positive glow extending right up to the anode. When these different portions of the discharge are separately tested, the region of the blue negative glow, especially the part nearest the cathode, is found to be by far the most effective in producing this active form of nitrogen and its yellow luminescence. When a Leyden jar is added to the secondary circuit the action is more intense and the blue glow greatly extended; the production of the active nitrogen is therefore greatly increased. If, now, the nitrogen be not allowed to remain in the Geissler discharge tube, but is drawn off into and through a second larger tube, both wider and much longer (a yard or more in length), the whole of this second tube is filled with a brilliant yellow glow, which persists for several minutes after the current is switched off. No electric discharge passes in this second tube, and the gas takes a considerable time to pass through it; the pressure is maintained at only a very few millimetres of mercury, and only $2\frac{1}{2}$ litres per hour of nitrogen need be used. The brilliant yellow glow is maintained so long as the discharge passes, and for several minutes after it is switched off.

If, now, acetylene gas be admitted to the second tube action immediately occurs between the nitrogen and the hydrocarbon, with complete alteration of the colour of the luminescence to lilac-purple, although, as is well known, ordinary nitrogen is quite inert. The substance produced is hydrocyanic (Prussic) acid HCN, by direct union of the two gases. But under the conditions of the reaction there is some dissociation, and the lilac glow is due to cyanogen, C_2N_2, the spectrum of which is given by the glow, both spectrum and glow resembling those of the cyanogen flame as seen when the gas is burnt at a jet in the ordinary preparation of cyanogen. The hydrocyanic acid can actually be isolated in a receptacle connected with the long tube, by freezing out with liquid air contained in a thermos tube surrounding the little receptacle. Or it can be drawn through a solution of sodium hydroxide, and the latter tested for the Prussian blue reaction by the addition of a mixed solution of a ferrous and a ferric salt, and acidifying.

Mercury reacts with this active nitrogen, either as liquid in the cold or when vaporised by warming in contact with the contents of the long second tube; in each case a nitride is produced, which on the addition of water affords ammonia, which yields the usual test reaction with Nessler's solution. The yellow glow becomes green and the mercury, if in the cold, becomes foul. Both the vapour and the foul substance, the nitride, give strong indications of ammonia with Nessler's solution.

Most hydrocarbon gases and vapours react similarly to acetylene, but neither oxygen nor hydrogen react directly as gases with the active nitrogen. The behaviour towards oxygen is, however, remarkable. A small quantity, only the $\frac{1}{750}$th part

[1] *Proc. Roy. Soc.*, A, 1913, *88*, 539; *Ber. der Deutsch. Chem. Ges.*, 1914, *47*, 2283; *Chem. Soc. Annual Report*, 1914, 49.

of the nitrogen present, renders pure nitrogen, which only glows faintly, brilliantly luminescent with the yellow glow; but two *per cent.* of oxygen destroys the glow absolutely. The purest nitrogen obtained, prepared by heating nitrogen from liquid air to 300° C. over sodium, still glowed, although not so strongly as the gas before purification by sodium, showing that traces of impurities do assist the glow, and presumably the formation of the active variety of nitrogen. This fact would appear to be akin to the well-known one brought to light by Prof. Brereton Baker concerning gaseous reactions, that a minute trace of water vapour materially assists, and may be indispensable, in these reactions. It also appears to be related to the fact already mentioned in this section on Luminescence, that the phosphorescence of hexagonal zinc sulphide is rendered more brilliant by the admixture with a small quantity of a chloride impurity such as common salt.

Optical Anomalies.—Anomalous optical behaviour, that is, the display of optical phenomena not in accordance with the crystal symmetry as indicated by the goniometrical investigation, assuming the results of the latter to be definite and unequivocal, is not an infrequent occurrence, and may be due to any one of several possible causes. The phenomenon of pseudo-symmetry, dealt with in Chapter LV., is not now alluded to, a phenomenon which consists in the display of optical properties corresponding to a higher system of symmetry than that really possessed by the substance, due to sub-microscopic parallel lamellar twinning. The chief cause of the anomalous optical behaviour now referred to is mechanical strain, which may be due to crystallisation at a high temperature and pressure and subsequent rapid or otherwise irregular cooling, or to the inclusion during crystallisation of minute quantities of foreign substances, generally minute crystals of other minerals, possessing different coefficients of expansion to that of the pure substance. Diamonds, which are probably produced both at a high temperature and under extreme pressure, are often thus under considerable internal strain, and frequently also contain minute crystals of foreign minerals as inclusions. Indeed, it is said (but see footnote on page 1146) to be quite common for a diamond to burst owing to the sudden relaxation of pressure, on its release from its matrix of blue clay. The researches of Moissan, Sir William Crookes, and Sir Andrew Noble have proved that the diamond does crystallise from carbon fused by the combined agency of a temperature somewhat higher than 4000° C. and a pressure of at least seventeen atmospheres; and that relatively rapid cooling from such a condition results in crystallisation with internal strain so marked that many such artificially produced small diamonds have burst while actually being examined under the microscope, and others that have not burst have exhibited strong signs of strain when examined between crossed Nicols. For diamonds, owing to this condition of internal strain, although of cubic symmetry and therefore theoretically isotropic, usually exhibit polarisation colours between crossed Nicols, this being the optical anomaly of the type now under discussion. Fig. 820 shows a group of ten diamonds of considerable size, uncut and quite colourless, arranged as an object slide for the projection polariscope. All these diamonds polarised in brilliant colours on the screen, the experiment having been

exhibited by the author both in lectures at the Royal Institution and in an evening discourse to the British Association during their meeting at Winnipeg in 1909, and afforded a striking example of anomalous double refraction as exhibited by crystals supposed to be isotropic. These ten diamonds, unspoilt by the lapidary, were generously lent to the author by the late Sir William Crookes, and are now in the Mineralogical Collection of the British Museum at South Kensington.

Another cause of optical anomalies is the occurrence of a fine lamellar structure, in which each lamella is a normally behaving crystal plate, but is not arranged parallel to its neighbours, neither is it arranged in a regularly reversed, alternated, manner with respect to its neighbours. All the effects and phenomena afforded by the artificial combination of thin doubly refractive crystal plates or films, such as by crossing at oblique angles as in the case of the mica films described on page 1102, are afforded naturally by "optically anomalous" crystals. In certain parts they show uniaxial properties, and in others biaxial characters, with varying angle of optic axes and position of the optic axial plane, indicating clearly that they are composed of thin lamellæ similarly crossing each other with more or less of regularity, and often with remarkable equality of thickness of the constituent films (see page 510). It is shown on page 508 that when absolute regularity of alternation occurs a higher mimetic symmetry usually results, that of a system higher than that of the single lamella; if the alternation be so fine as to be sub-microscopic, pseudo-symmetry according to a higher system may be assumed, such as that of potassium sulphate above 600° C. (hexagonal, whereas ordinary potassium sulphate is rhombic), which it is practically impossible to distinguish from a polymorphous conversion. When, however, this regularity of repeated twinning is absent, optical anomalies of a most perplexing character may occur, which require special investigation in every case met with.

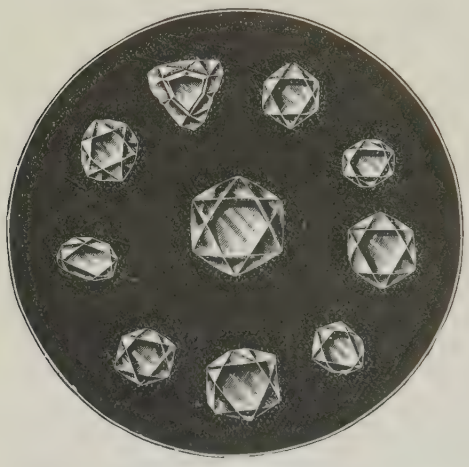


FIG. 820.—Ten Diamonds with Natural Faces arranged to show Strain Colours in Polarised Light.

Yet another cause for the appearance of double refraction in an isotropic substance is the admixture with a small quantity of an isomorphous substance, the molecular volume and topic axial ratios of which are considerably different to those of the pure substance. For instance, Brauns has shown that alum crystals frequently show double refraction when the alum forming the crystal is not one pure double salt of the alum group, say potassium aluminium alum, but is a mixture of a large proportion of

this with a small quantity of another alum, say ammonium aluminium or ammonium chrome alum ; whereas Brauns never observed any double refraction, with its accompanying polarisation in colour, whenever the alum crystal was that of a single pure member of the group of alums.

These facts indicate the necessity for extreme care in preparing absolutely pure crystals of any artificially prepared substance undergoing investigation ; and also the desirability of investigating, whenever possible, the state of purity of a naturally crystallised mineral substance, and the existence or otherwise of minute enclosures in the crystals, whenever anomalous optical properties are experienced.

As regards external deforming forces acting on crystals, experiments have shown that, in general, whenever external physical force is applied to a crystal, except under the special circumstances of absolutely equal pressure in all directions, such as that involved in the relatively slight changes of atmospheric pressure, deformation of the homogeneous crystal structure occurs, with the inevitable alteration in the optical phenomena. If the crystal be normally isotropic, it will in general become doubly refractive under irregularly and locally applied pressure. It is only, however, when permanent deformation occurs, the elastic limit being overstepped, that the anomalous optical behaviour persists ; and the persistence will probably also be equally local, and not consist in any definite conversion of the whole body of the crystal into one of apparently different symmetry, but only that portion where the deformation is permanent.

The effect of local pressure or internal strain is not only effective in rendering an isotropic cubic crystal apparently doubly refractive, but is well known to be capable of producing double refraction and brilliant polarisation in non-crystalline transparent substances such as glass and jelly. The polarisation colours and figures afforded by chilled glasses, that is, glasses rapidly cooled instead of being carefully annealed, and therefore in a violent state of internal strain, are familiar examples. The author possesses a thick plate of glass of circular shape, a squat cylinder about half an inch deep and one inch in diameter mounted as a slide for the projection polariscope, which affords between crossed Nicols in parallel light a brilliant figure filling the whole disc on the screen, composed of black cross and circular spectrum rings, which cannot be distinguished from the figure afforded between crossed Nicols in convergent light by a uniaxial crystal. The strain in this case happens to be symmetrical to the axis of the cylinder, which thus behaves as an optic axis.

Optical Phenomena with Spherulites. — From glassy viscous liquid "melts," both natural (lavas and internal igneous semi-liquid masses) and artificial (slags, glasses, etc.), we frequently obtain spheroidal crystallisations composed of radially arranged bundles of acicular crystals. A plate cut to pass through the centre of such a spherulite shows between crossed Nicols—whether the elongated individual crystals are uniaxial with the length parallel to the axis, or biaxial with the length parallel to one of the three axes of the optical ellipsoid—a black cross, the arms of which are parallel to the directions of vibration of the Nicols, while

the spherulite is brightly illuminated at the 45° intermediate positions. The cross is distinguished from that of a uniaxial crystal by the fact that it is afforded in parallel light, whereas the uniaxial interference figure is produced only in convergent light. The cross also moves with the spherulite when the object-section is moved, whereas the interference figure is immovable on sliding the section in its own plane. The phenomenon may be imitated by attaching to a rotating disc, out of which a radial slit has been cut, a single crystal of a uniaxial substance, which extinguishes parallel to its length, and rotating the disc rapidly between crossed Nicols. The additional colour effects produced when the substance happens to be pleochroic have already been referred to on page 1120.

An excellent example of this spherulitic radial structure is afforded by the glucoside salicin, $C_{13}H_{18}O_7$, the beautifully transparent radial spherulites of which, resembling wheels and their spokes, polarise between crossed Nicols with exceptional brilliancy and variety of colour, in the sectional portions intervening between the black arms of the cross. Rotation of the analysing Nicol is followed by a similar rotation of the cross. The effect of interposing a half-wave mica plate between the crystal-slide and the analyser is to reverse the sense of rotation, which is then contrary to the direction of rotation of the analyser (see p. 910 for experiment by J. R. Rendel involving this effect). To prepare a slide of salicin for the microscope or projection polariscope, the substance should be dissolved to saturation in a mixture of one part of alcohol to four parts of water; a thick layer of the liquid is poured over the micro-slip or circular glass plate, and evaporated rather rapidly with warming so as to effect the labile crystallisation, which is productive of the spherulite radial groups instead of the metastable production of rhombic tabular crystals. A little practice is required to obtain the best results, especially as regards the degree of heat to be employed in the evaporation on the slide, and as to the precise moment to cease warming. When successful, the whole slide is covered with the exquisite transparent and quite colourless circular radial groups, of a more or less equal diameter, which for the lantern polariscope may conveniently be as much as half a centimetre. Such a slide is illustrated in Fig. 666*a* on page 910.

Note on Optical Anomalies of the Diamond.—In a communication to the Mineralogical Society on June 21, 1921, Dr. Sutton, of Kimberley, South Africa, stated that the inclusions in diamonds are chiefly minute garnets and cubes of iron pyrites, and as their faces and edges are wonderfully perfect and their melting-points not excessively high the temperature of formation of the diamonds including them cannot have been inordinately high. He considers that the element of prolonged time as a factor in diamond formation has not received adequate attention. He discountenances the stories of bursting natural diamonds, and stated that in his very long experience at the Kimberley mines he had not known an authenticated case. Instead of bursting, what does often happen is that the difference of expansion of the inclusions and the diamond causes splitting of the latter along the octahedral planes of perfect cleavage. Sir William Crookes, however, in his book *Diamonds*, page 120, records an actual case of an artificial diamond bursting during the night, after being mounted on a slide for microscopic examination, and covering the slide with minute fragments.

CHAPTER LII

THE CRYSTALLOGRAPHIC MICROSCOPE AND ITS ACCESSORIES

The polarising microscope is one of the most useful and important instruments of the crystallographer's laboratory. For although all the optical constants are measured eventually by the instruments described in preceding chapters, constructed specifically for each particular purpose, provided adequately large crystals can be obtained for a complete investigation, still the microscope is a sort of *multum in parvo* of them all, most convenient for preliminary work, and the last resort in all cases where crystals cannot be procured of the necessary size (minimum, that of a pin's head) for individual measurement of each constant on its own specific measuring instrument. Moreover, the crystallographic microscope is invaluable in all work of a petrological character, such as the study of the natural crystal-sections revealed in the thin slices of rocks specially prepared for examination under the microscope, for the study of the minute crystals obtained in micro-chemical analysis, or for that of excessively small crystals alone obtainable by any process, for rapid work on the optical characters of larger crystals for identification purposes, and lastly, in carrying out a preliminary examination of the more apparent optical properties of a new crystalline substance. Fortunately, this country has for many years excelled in the construction of microscopes and their objectives and other accessories, and the late Mr. James Swift made for his firm of James Swift & Son a world-wide reputation for petrological microscopes, a just reputation which is now being added to by his son as regards the construction of microscopes suitable for all varieties of crystal work. Messrs. R. & J. Beck, largely owing to the ability of Mr. Conrad Beck, also now construct excellent microscopes, and have produced some especially good objectives. Also, the continental firms of Fuess of Berlin, Voigt & Hochgesang, now taken over by Steeg & Reuter of Homburg, Zeiss of Jena, Nachet of Paris, and the Société Génevoise, are all constructing admirable instruments for this specific purpose. The Bausch & Lomb Optical Co., of Rochester, N.Y., U.S. America, are likewise now also constructing some excellent instruments.

The best crystallographic microscope which has come within the author's own experience is the large pattern one constructed by Messrs. Swift & Son, designed in its earlier form by Mr. Allan B. Dick, and known

as the "large Dick microscope." With the subsequent additions which have been made to this instrument on the recommendations of Sir Henry Miers, Professor Bowman, Mr. G. W. Grabham, and the author, this instrument is in every way admirable for the crystallographer's purposes. It is

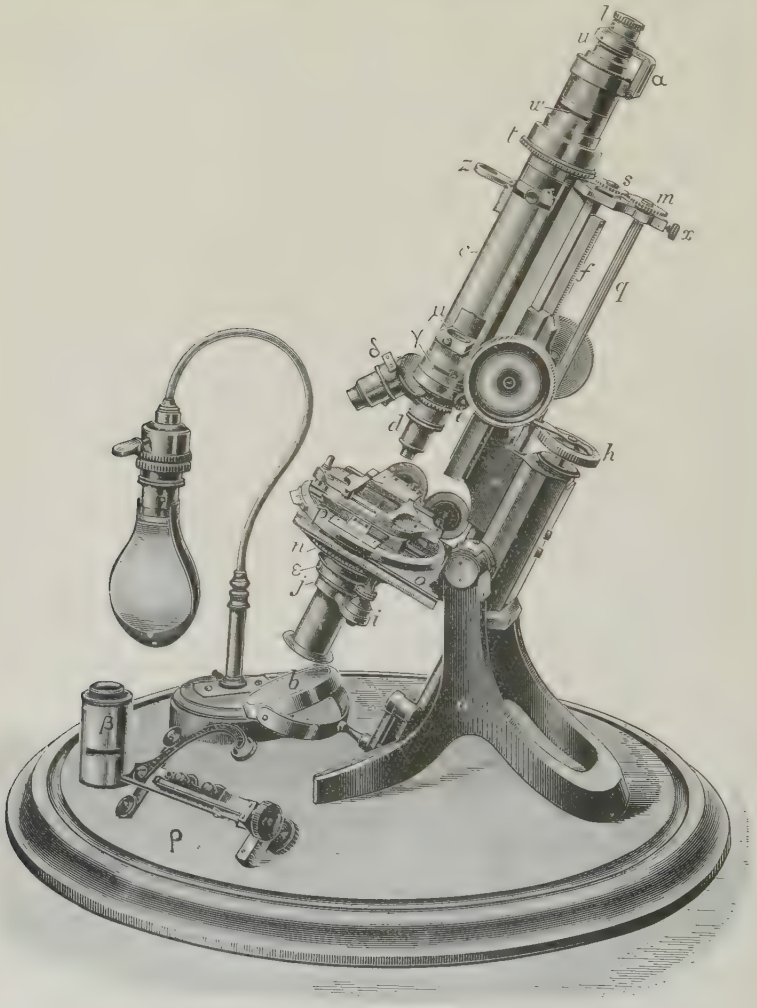


FIG. 821.—The Dick Crystallographic Microscope constructed by Swift, fitted with Measuring Stage.

shown in Fig. 821 in its completest form for ordinary work, with the measuring stage, which includes both a rotating divided circle of great accuracy and two rectangular measuring movements; in Fig. 822 as fitted for work with the Miers goniometrical stage: and in Fig. 823 as arranged horizontally with the latter for optic-axial-angle measurements in a highly refractive liquid.

In Fig. 824 it is also shown upright in its simplest form, with the fixed rectangular stage more clearly revealed, and Swift's mechanical stage or micro-slip-holder, for holding, and rapidly moving over the stage, the ordinary 3 × 1 inch slips bearing rock-sections or other mounted crystals. Lastly, in Fig. 825 the instrument is shown with additional accessories devised for special work by Mr. Grabham.

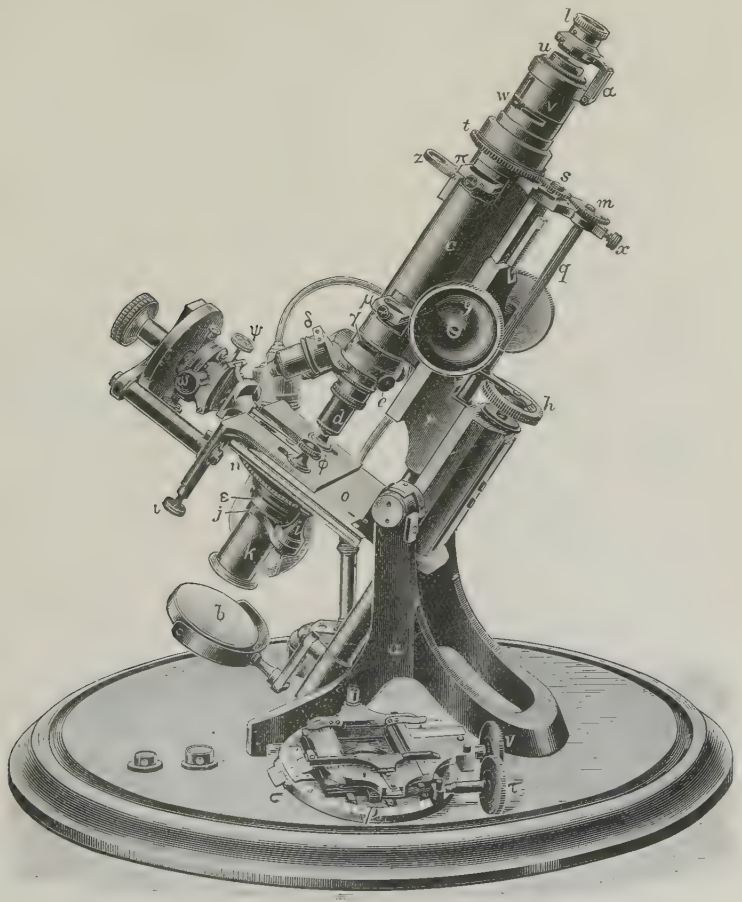


FIG. 822.—The Dick Microscope fitted with the Miers Stage Goniometer.

The instrument has a particularly convenient and graceful form of stand, *a* in Figs. 821 and 822, which carries between its claws the plano-concave double mirror *b*, provided with two rotatory axial motions and two movements of transference, for adjusting the illuminating light reflected by the mirror so as to pass exactly along the axis of the body-tube *c*. The objective *d* is provided with a centring adjustment above the standard screw attachment, manipulated by two screws *e*. The coarse adjustment by rack *f* and pinion *g*, and the fine adjustment manipulated by the divided milled head *h*, act with great smoothness and precision, without any backlash, owing in the one

case to obliquity of the rack teeth, and in the case of the fine adjustment to a strong pressure-maintaining spring. This fine adjustment depends on a differential screw, with which in the case of the instrument possessed by the author the greatest possible care was taken in the turning, and which, with the aid of the divisions on the top of the milled head, reads to the thousandth of a millimetre of axial movement of the microscope. It is of special use in determining thicknesses by the refraction method. The coarse adjustment is also graduated, a silver scale, shown in Fig. 824, divided directly into half millimetres being carried by the supporting bracket, and a silver vernier carried by the body-tube enables it to be read to a fiftieth of a millimetre.

A principal feature, introduced by Mr. Dick, and since adopted on most modern instruments, is that the polarising and analysing Nicol prisms *k* and *l* may be rotated

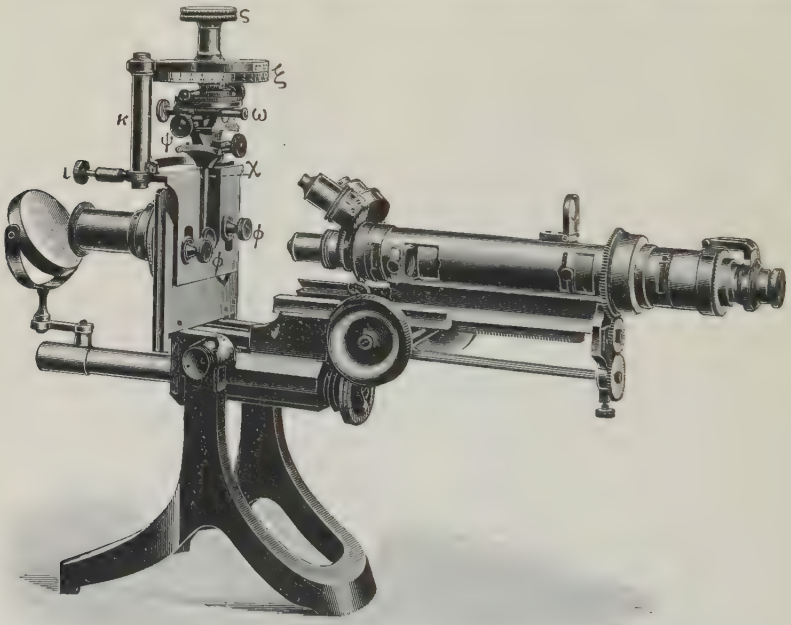


FIG. 823.—The Measurement of Optic Axial Angles with the Dick Microscope and Miers Stage Goniometer.

together from the upper end of the microscope by the toothed wheel *m*, or from below the stage by means of the large milled disc *n*, the fundamental stage *o* being fixed, and of rectangular shape. Hence, instead of rotating the crystal with its stage, which is not always convenient, the crossed Nicols may be rotated simultaneously, in which case the rotating stage *p* in Fig. 821 is not required. The amount of the rotation is registered by a silver divided circle carried by the large milled disc *n*, seen in Fig. 824, a vernier also on silver being carried alongside it by the fixed stage, at the bottom of a recess cut and scooped out of the latter for the purpose of revealing the graduations of this circle, and for convenience of manipulation of the crystal-holder of the goniometer stage as shown in Fig. 823. The gear for effecting this simultaneous rotation of the Nicols is very simple. The toothed wheel *m*, which is smoothly made so that it may also act as a milled head for rotation by the hand, is carried at the upper end of a steel fluted shaft *q*, which passes without contact through a boring in the body

bracket r; a similar toothed wheel is also carried at the lower end of the shaft under the fixed stage. With the aid of an intermediate smaller toothed wheel s in each case, the upper and lower wheels each gear with a larger one t, which is really only an annulus, the centre being perforated in both upper and lower wheels with the full aperture of the optical tube and stage opening respectively. For the upper one is concentric with the optical tube at its upper end, and rotates about the tube and its axis in a plane perpendicular to the latter, carrying with it all the upper fittings including the eyepiece u, its outer tube v, which has a slot w for quarter-wave mica or other insertions, and the analysing Nicol prism l. The Nicols can be fixed at any desired position by means of the little clamping screw x. The lower large wheel under the stage carries with it, below, the large milled disc n which bears the silver divided circle on its upper surface, the divisions being single degrees; the vernier carried by the fixed stage enables the readings to be carried out to minutes. The circle may be conveniently read by a lens z hinged, at a convenient height for focussing, to the front of the body-tube. Both wheel and circle plate are perforated with a wide central aperture to permit of the passage of the light rays, and of the insertion of a sub-stage condenser when required. To this annular disc n the polarising Nicol prism k is fitted, a short column i proceeding downwards from near the margin of the disc and carrying at right angles at its lower expanded extremity a rotatable arm terminating in a ring j, in which is fixed the outer tube-case of the polarising Nicol and in which the latter and its inner mount-tube are rotatable. The pivoting of the arm about the column is so arranged, by means of a stop-pin, that the Nicol is placed exactly in position in the optic axis of the microscope when the arm is at one end of its possible swing, and is conveniently out of the way when at the other end of its swing.

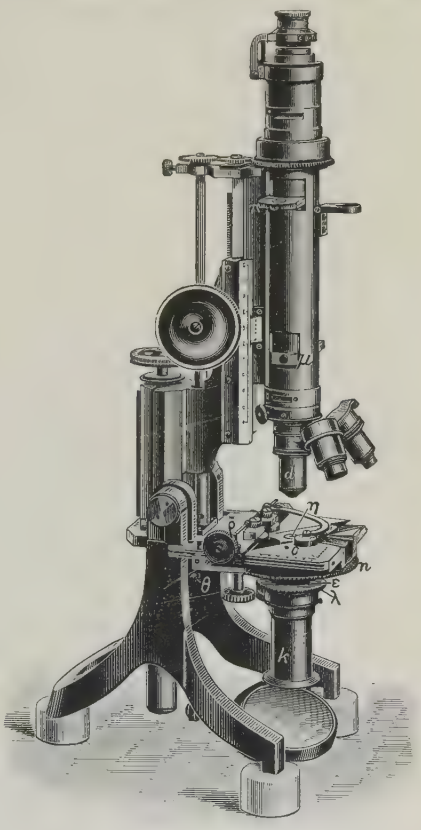


FIG. 824.—The Dick Microscope with Swift Mechanical Stage.

The polarising Nicol is larger than usual on the author's instrument, having a clear minimum aperture of $\frac{7}{8}$ths of an inch. It has a bevelled graduated circle and an indicator on the outer tube; a spring claw also falls into a shallow notch with a click when exact crossing or parallelism of the Nicols is attained. The analysing Nicol l is also carried by a double elbow arm a, hinged so that the Nicol can be rotated backwards out of the way when not required, or when it is desired to insert a different eyepiece. The Nicol itself is provided with a bevelled divided circle and indicator, and is separately rotatable, a notch and spring click like those of the polariser being also provided to indicate the crossed and parallel positions even when the light is shaded off. Hence, the two Nicols can either be rotated separately as

in the ordinary polarising microscopes, or together, mutually crossed or parallel, or in any desired position with respect to each other's planes of polarisation, by means either of the milled disc n or the toothed wheel m. As the eyepiece rotates with the analyser, the cross-wires (spider-lines) carried by it also simultaneously rotate. The eyepieces are of the form shown at β resting on the base-board in Fig. 821, and a projecting pin near the upper end of each eyepiece tube fits into a notch cut in the rotating tube in such a position that the cross-wires are parallel to the planes of polarisation and vibration of the Nicols. Each eyepiece also has a slot corresponding to that (w) in the rotating tube, for the insertion of the quarter-wave mica plate or quartz wedge, the slot in the tube being covered by an outer shutter-tube when the latter are not required. A similar pair of slots with covering shutter-tube are provided at γ just above the centring apparatus.

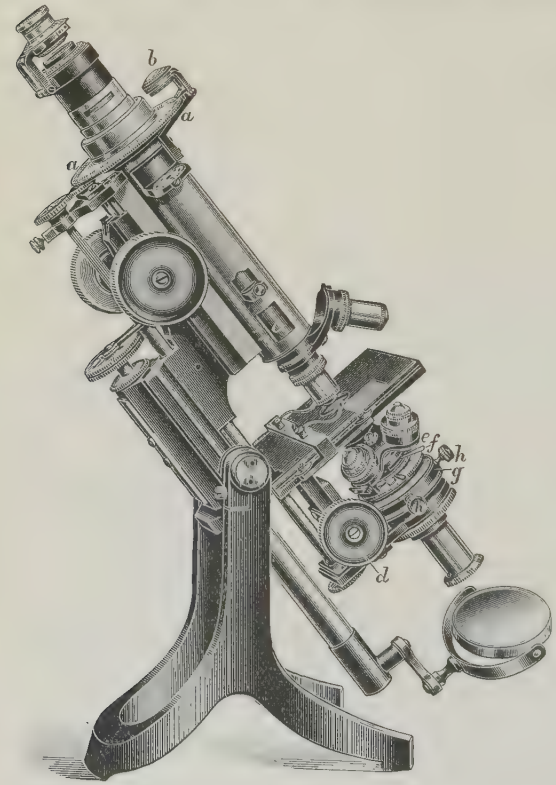


FIG. 825.—The Dick Microscope with Grabham Sub-stage Fittings.

A nose-piece δ for three objectives is provided. The following three are the most useful objectives for crystal work and should be left on the nose-piece as a rule, namely, a 1½-inch objective, for rock-section work or the preliminary examination of ordinary goniometrically measurable crystals; a 1-inch objective for parallel light work with crystals just too small for goniometrical investigation in the ordinary way; and a ¼-inch objective for convergent light work. It is, of course, very convenient to possess a greater range of objectives than these essential ones, and those for which the author has found most use in addition to the three mentioned are a 3-inch, 2-inch, ½-inch, ⅛-inch, and $\frac{1}{12}$-inch, all dry lenses, and a $\frac{1}{12}$ oil-immersion lens.

A specially good ¼-inch objective, shown in position in Figs. 823 and 824, marked d in the latter, is supplied by Messrs. Swift for use with convergent light, acting as the collecting lenses of the system. The converging lenses consist of a sub-stage condenser ϵ and an additional lens η in Fig. 824, to complete the convergence when necessary, as it usually is; this lens η is carried in the central line but nearer one end of a bevelled slider let into a corresponding dovetailed groove cut diagonally in the top of the rectangular fixed stage o. This slider can be pushed along so that the lens η is brought into or out of position by means of the little knob-handle θ belonging to an arm attached to the slider underneath the stage; an aperture 21 millimetres in

diameter, the same as that of the stage aperture itself, is also made in the slider, and this open aperture is centrally placed when no additional lens is required, and is always in position when the microscope is being used for parallel light observations. The sub-stage condenser is altogether removable when desired, screwing directly into the fixed stage, the central aperture of which is tapped with a corresponding screw thread to that carried at the top of the condenser tube. The achromatic condensing lens system is carried in a short inner tube sliding within the latter; a pin projecting from the inner tube fits in a vertical groove in the outer tube to prevent rotation of the lenses, and by means of a third outermost freely rotatable tube—carrying a large milled flange λ for convenience of effecting the rotation, and the inner bore of which has a spiral groove, into which the pin of the inner lens tube also falls—the condensing lens system can be raised or lowered nearer to or further away from the stage. Its normal position for use along with the additional stage-lens η is almost at the upper extremity of its path, quite close to the lens η. This vertical adjustment of the condenser is also very convenient when the latter is being used for ordinary microscopic sub-stage condenser work. An iris diaphragm, particularly useful in the latter operations, is also fitted at the lower end of the fitting, its opening being varied by means of a small handle projecting from and moving in a slot. The polarising Nicol k comes into position immediately below this diaphragm. The large size of this Nicol enables a particularly well-lighted field of interference bands to be obtained, with a crystal plate perpendicular to the first median line on the stage, excellent for photographic purposes.

The complementary collecting lens system consists of the $\frac{1}{4}$-inch objective d and a plano-convex Bertrand lens mounted in a slider μ in the body-tube c; the slider has two apertures, each of 17 millimetres diameter, one filled permanently by the Bertrand lens, and the other either left empty or filled with a removable Biot quartz plate, 3·75 millimetres thick and cut perpendicularly to the axis. This is the correct thickness and orientation to give, with parallel Nicols, the violet transition tint between the first and second order spectra, for use as described on p. 1105 of Chapter L. The slider is inserted in a short inner tube sliding up or down within the body-tube c, which latter is cut away here for the width of the slider and for rather more than the same height. This enables the Bertrand lens to be adjusted, by sliding up or down the body-tube, so as to obtain the clearest definition of the interference figure. A second Bertrand lens is also provided in another slider π higher up the body-tube c, and this one has fitted over it a little circular diaphragm pierced with six apertures of different diameters, the largest being 3·5 millimetres and the smallest 0·7 mm. The slider is fitted in an adjustable tube sliding in the body-tube, which is cut out for the width of the slider, as in the case of the lower one; the slider has also a second open aperture, which is in position when the Bertrand lens in the other aperture is not required.

The lower Bertrand lens is that usually employed for the production of interference figures. Together with the $\frac{1}{4}$-inch objective, and with both the sub-stage condenser and the additional lens η on the stage slider in position, it affords a magnificent interference figure with a crystal-plate cut perpendicularly to the acute bisectrix of the optic axial angle of a biaxial crystal or normally to the optic axis of a uniaxial one. The upper Bertrand lens gives a much smaller but very clear interference figure; it is intended for use with a small crystal, say a particular one in a rock section.

The course of the light rays in the microscope thus used as a "conoscope," or convergent light polariscope, is essentially as follows. The more or less parallel rays from the mirror at the foot of the microscope are rendered convergent by the sub-stage condenser, and still more so by the hemispherical or very short focus lens of the stage-slide. They then pass as a highly convergent cone through the crystal-plate, the apex of the cone being in the centre of the crystal when the adjustment is ideal, to the $\frac{1}{4}$-inch objective, which collects them and brings about the formation of the interference image, which is about 5 millimetres in diameter, just above. This primary real image is then reproduced by the Bertrand lens as a secondary real image just below the

eyepiece, and this is magnified by the eyepiece as a large virtual image, of which the apparent plane is just below that of the secondary real image.

Stage Fittings.—Three important stage fittings are provided, which are readily attached when required, the two ordinary spring-clips for holding microscope slides on the fixed rectangular stage being easily removable, as they are simply carried by pegs fitting into two cylindrical holes in the stage.

The first is a simple **Mechanical Stage** for rapidly moving an ordinary 3-by-1-inch microscope object-slide about on the stage, so as to bring the desired object quickly into the centre of the field. It is shown at ρ lying on the mahogany base-board in Fig. 821, and in position in Fig. 824. It consists of a narrow brass bar which slides over the fixed stage by means of two roller-wheels on a T-piece carried at one end of the bar, and which roll in a V-shaped groove in one side-edge of the stage, close contact and motion being both obtained by means of a short fluted cylindrical rod terminating in a milled head, resembling a screw in appearance but with flutings instead of a helix, which is carried at the other end of the bar so that the flutings may revolve, with sufficient friction to effect the movement of the whole mechanical stage, in corresponding closely parallel grooves in the other side of the fixed stage; the fluted rod is pivoted on a short arm pressed inwards by a spring, thus maintaining close contact of flutings and grooves. Rotation of the milled head causes the mechanical stage with its micro-slip to traverse the fixed stage in a direction parallel to the sides of the latter. Movement of the micro-slip in the direction rectangular to this, parallel to its own length, is effected by three rollers, one of which is carried freely at the end of a curved arm, and is maintained pressed against the micro-slip by a strong straight spring screwed at one end to the bar and pressing against the arm end, which is so shaped that a little force has to be expended in order to open out the bent arm sufficiently to insert the micro-slip in position, between the free roller at the end of the arm and the two other rollers, the force of the spring retaining it then in that position. The other two rollers are carried by the bar itself, which is here bridged over them sufficiently to give them free play when rotated; the rotation is effected by means of a second milled head at the end of a steel shaft, on which, opposite the two roller axles, are two portions of the thread of an endless screw, which gear with worm wheels carried on the axles. Rotation of this shaft by its milled head thus effects movement of the micro-slip in the direction of its length, while rotation of the other milled head with fluted axle moves the slip perpendicularly to its length.

The second is a **Measuring Stage**, a rotating stage with divided circle, and two divided rectangular measuring movements. It is shown lying on the base-board at σ in Fig. 822, and in position in Fig. 821. This stage is intended for use when the ordinary manner of rotating the crystal is desired to be employed, instead of the simultaneous rotation of the Nicols and cross-wires, and also for the accurate measurement of lengths in two rectangular directions. The lower circle carries two projecting screw-pegs which fit into two holes in the rectangular fixed stage of the microscope, and when the whole fitting is laid on the latter with the two pegs in their holes it can be secured, and the lower circle thus rendered a fixed one, by screwing two milled-headed nuts from below on to the threads of the pegs. The rotatable circle p has a silver bevelled limb divided directly into degrees, and a silver vernier carried by the fixed circle enables the readings to be made to 5 minutes of arc. The two rectangular movements are effected by rotation of the large milled heads τ and υ, and each movement bears a silver scale divided directly into half millimetres, and reading with the aid of a silver vernier to the fiftieth of a millimetre, 0·02 mm. The upper movement is furnished at the top with a sliding object-slip holder, provided with tension springs for secure gripping of the slip. The whole of the movements are constructed to work very smoothly without backlash, and afford all that is required for either circular or rectilinear measurement, the combination enabling the latter to be carried out in any azimuth. When it is desired to use convergent light with this stage, which is but rarely, as its

chief uses are with parallel light, a duplicate convergent system, equal to the sub-stage condenser and the stage lens together, is provided. It is mounted in a second but much longer inner tube sliding in the sub-stage fitting just like the ordinary sub-stage condenser, having a guiding pin gearing with the slot of the fitting. The top lens can be brought by rotation of the milled flange λ (Fig. 824) flush with the surface of the measuring stage, or adjusted at any position below this.

The third is a **Stage Goniometer,** which is shown in position in Fig. 822, and as used with a cell of immersion liquid, and the microscope consequently arranged horizontally, in Fig. 823. It is a small Miers goniometer specially adapted by him to the microscope stage, to which it is screwed by two milled-headed screws ϕ passing through wide slots in the stage-plate of the goniometer, broad washers being provided to cover the slots; a considerable amount of adjustment is thus permitted in the fixing. The stage-plate is cut away largely at its central part, in order to permit of the introduction of a circular cell for the highly refractive liquid, and also to afford free play to a long needle-shaped crystal-holder χ, carried axially at the end of the adjusting and centring movements ψ and ω of the goniometer. The fixed stage of the microscope, as already mentioned, is also cut away and scooped out in a conical manner to give full room for the play of the crystal-holder. The short rectangular elbow bracket of the stage-plate is attached to the goniometer by two columns κ, about one of which, hidden in the figures, it is pivoted, while the other column is attached in a slot in the bracket in such a manner that its position in the slot may be varied by a piston screw with milled head ι, a strong spring, curved so as to be well out of the way of the adjusting movements, maintaining the column and piston in rigid contact. This enables the whole goniometer to be moved, until the crystal-holder (the needle, to the end of which the crystal is attached by goniometer wax) is quite clear of the fixed stage of the microscope and its conical depression, in all positions during rotation of the goniometer circle ξ by means of the large milled head s. The circle is divided directly into half degrees, and reads with the aid of the vernier to single minutes.

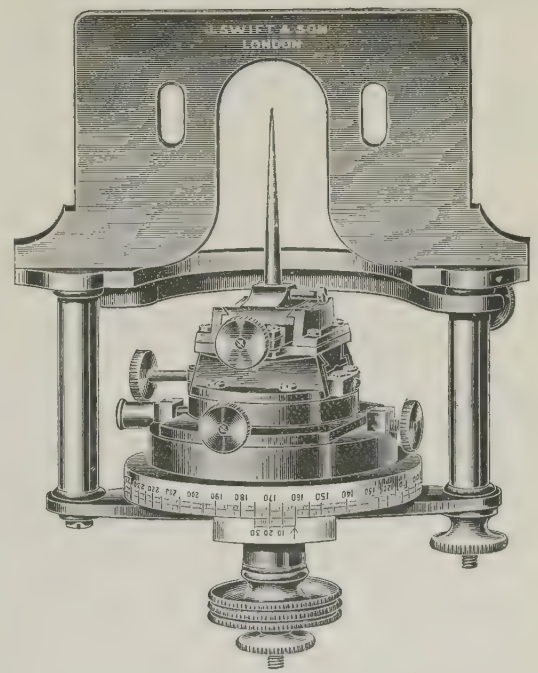


FIG. 826.—The Stage Goniometer.

The stage goniometer shown in Figs. 822 and 823 was constructed by Messrs. Troughton & Simms. In Fig. 826 is shown a similar stage goniometer constructed by Messrs. Swift, with modifications on that of Sir Henry Miers introduced by Prof. Bowman, largely for the purpose of strengthening the parts and obtaining greater freedom of movement. Its construction will be quite clear from the figure.

Some further additions and modifications have been introduced into the Dick crystallographic microscope by Mr. G. W. Grabham, and the instrument embodying them, as supplied by Messrs. Swift, is shown in Fig. 825. In the first place the divided circle rotating with the Nicols, and divided to read with the vernier to 5′, is placed at *a*, just below the eyepiece fittings, and is read by a lens *b*. In the second place an alternative analysing Nicol is fitted at *c* in the body-tube between the objective nose-piece and the Bertrand lens; it may be pushed in or pulled out of position with the aid of a little handle-rod on the other side of the instrument and therefore not shown in the figure. This is for use in the older way still preferable in many kinds of crystal work, and with which the rotating stage shown in Fig. 821 is so useful. The third feature is a focussing adjustment, by rack and pinion *d*, to the sub-stage, and the provision of a triple revolving-piece *e* carrying the battery of three different condensers, any condenser having the Royal Microscopical Society's standard screw being able to be attached to one of the three apertures of the piece just as any objective with the standard screw may be fitted to the nose-piece of the Dick microscope. An iris diaphragm *f* is provided as in the ordinary Dick instrument already described. A cell *g* for the reception of any one of a variety of stops for oblique and dark ground illumination is also provided, on a swinging arm, the mode of mounting also permitting of the rotation by the handles *h* of the cell and the stop it may contain. This arrangement is of great use in observing the shadow effects specially investigated by Becke, and which are indicative of the relative refractive indices of adjacent crystals in a rock section. A selenite or mica plate may also be fitted in this cell.

The three condensers found most useful are the Swift oil immersion of numerical aperture 1·40, the Swift dry condenser of unit numerical aperture, and a low-power lens for producing weak convergence. When parallel light is desired the latter lens is removed, and as the other two condensers give most of the necessary variety of angular field required this may conveniently generally be the case, so that the observer can change from parallel light to either degree of convergence instantly.

The instrument is otherwise like the ordinary Dick model already described.

Accessory Fittings to the Polarising Microscope.—There are a number of very useful and important accessories, which may be attached to either form of the Dick microscope. Their description will now be given.

The Ramsden Micrometer Eyepiece.—This is a positive eyepiece, composed of two plano-convex lenses with the convex surfaces inside facing each other, as shown in the section given above the general view of the micrometer in Fig. 827. The focus is outside the combination, fairly close to the second (larger) lens, the closeness depending on the power of magnification, which of course again depends on the curvature of the convex surfaces. The combination thus behaves as a single lens, but is better than the latter as the spherical and chromatic aberrations are largely corrected. It focusses not only the real image formed by the objective at the top of the microscope body-tube, but at the same time the spider-lines of a micrometer with

drum-headed screw, arranged in the plane of the image afforded by the objective. The whole arrangement is shown in Fig. 827.

The lens combination is carried in its own inner tube, which is adjustable, by sliding in an outer one attached to the top of the micrometer box, so as to focus both the spider-lines and the "comb" or scale of saw-like teeth and notches in a metallic plate, which forms a horizontal chord across the circular field (the plate cutting off the lower segment) somewhat below the centre, as shown in Fig. 891 in Chapter LVII. Every fifth notch is deepened, and from the central one, marked by an expansion of the notch at the bottom into a circular aperture, the fixed spider-line is stretched vertically across the field. A second movable spider-line, parallel to the first, is carried by a sliding frame, the movement of which is effected by the very fine micrometer screw of $\frac{1}{100}$-inch pitch, the drum and milled head of which are seen on the right of the micrometer box in Fig. 827. The silvered drum is divided into 100 parts, every tenth being numbered and every fifth elongated. An indicating mark also on silver is carried by a projection from the box When the spider-lines are coincident

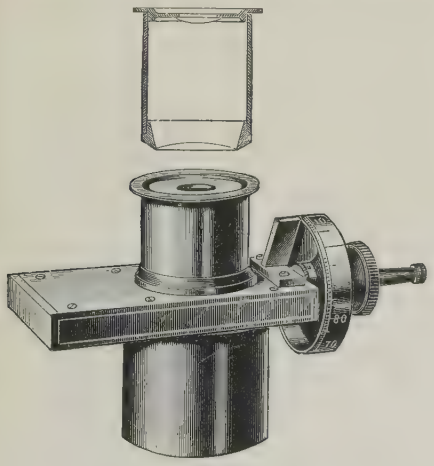


FIG. 827.—The Ramsden Micrometer Eyepiece.

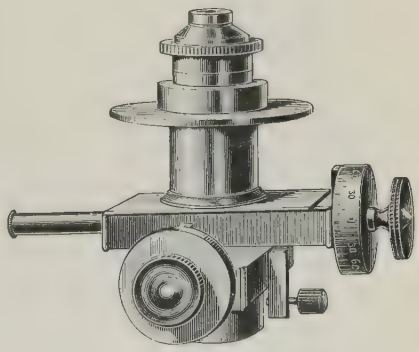


FIG. 828.—The Wright Double Micrometer.

(one really just clearing the other in front but appearing coincident as seen through the eyepiece) the reading is 0°, and 100 drum divisions, one complete revolution, correspond to one notch of the comb, and about a fiftieth of a field diameter. Hence, the micrometer reads to the $\frac{1}{10,000}$ of an inch. The wider lower tube below the micrometer box fits into the body-tube of the microscope.

The Wright Double Micrometer.—A micrometer on Ramsden's principle, but in which there is a second movable spider-line arranged at right angles to the ordinary one, the movement being measured in a precisely similar manner by means of a second screw with divided drum-head, is recommended by F. E. Wright for use in connection with Becke's methods of investigating crystals under the microscope, and is shown in Fig. 828. Its mode of employment will be fully discussed in the next chapter.

The Goniometer Eyepiece.—This is an eyepiece with rotatable spider-line and corresponding circle, shown in Fig. 829. The divided silver circle reads to 2° directly, and is fixed to a broad flange attached to the top of the lower tube of the eyepiece, and with the silver vernier carried on the rotatory bevelled plate attached to and moving with the upper narrower eye-tube reads to half degrees. In the focal plane of the eye-lens, seen in section in its adjustable tube above the general representation of the eyepiece in Fig. 829, and in the same diametral line with the zero division of the

vernier, a spider-line is stretched, which thus revolves with the vernier, while a second spider-line is permanently fixed diametrically from the 0° to the 180° graduation of the fixed circle, also practically in the focal plane, room being just left between the two lines for the one to rotate without touching the other. The lenses are arranged on the ordinary Huyghenian principle to be described in the next paragraph, as a negative eyepiece, and the focal plane of the spider-lines is that of the front, or eye-lens. It is important that this eye-lens should be mounted separately in its own tube, sliding fairly tightly in a fixed outer tube, so that it may be adjusted to suit the observer's own eye and enable a perfect focus of the spider-lines to be obtained. This goniometer eyepiece thus enables the angle to be directly measured between any pair of crystal faces (on a tabular crystal) which are perpendicular to the plate and the microscope stage, thus forming the boundary faces of the plate and appearing completely foreshortened as its edges. The fixed spider-line is laid parallel to, or better coincident with, one of the edges, and the movable spider-line is adjusted to coincide with the other. The crystal-plate must also be brought so that the corner formed by the intersection of the two edges is coincident with the intersection of the two spider-lines. The angle between the two faces is then at once given by the reading of the circle of the goniometer eyepiece.

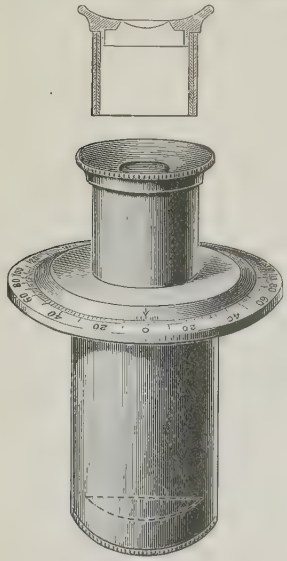


FIG. 829.
The Goniometer Eyepiece.

The **Huyghenian Eyepiece** provided for ordinary work with the microscope is shown in Fig. 830, and its arrangement of two plano-convex lenses will be clear from the figure, in which they and the diaphragm between them are represented by dotted lines. The two lenses both have their plane side facing the observer, contrary to the method of the positive eyepiece. The image is formed between the two lenses instead of outside both, and the whole arrangement is called a negative eyepiece. The larger lens further from the eye is known as the field lens, as it produces an image of the microscope field between itself and the eye-lens, which the latter then observes and enlarges. A diaphragm carrying the crossed spider-lines is arranged at the focal plane. It is imperative that the eye-lens be mounted, as just stated, in its own inner tube, readily capable of sliding adjustment so as exactly to focus the spider-lines. The Huyghenian eyepiece has the great advantage of giving a wide field. The actual form given to it in the Dick microscope is shown at β (the eyepiece on the base-board) in Fig. 821. The goniometer ocular just described is a special application of it, and another will be described in the next paragraph.

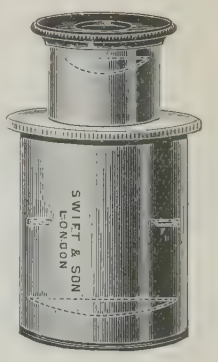


FIG. 830.
The Huyghenian Eyepiece.

The Bertrand Quartz-plate Eyepiece—This is a Huyghenian negative eyepiece with a special compound quartz plate in its focal plane between the two lenses. Its appearance is just like that of the ordinary eyepiece, and while the latter is in position at the top of the body-tube in Fig. 821 the Bertrand eyepiece is the one marked β lying on the base-board. The Bertrand eyepiece is employed for stauroscopic purposes, instead of a Calderon double plate of calcite, that is, for the enhancement of the sharpness and accuracy of determinations of extinction. In the place of the crossed spider-line diaphragm

of the ordinary Huyghenian eyepiece a composite plate of right- and left-handed quartz, known as a "Bertrand quartz plate," is fitted. The arrangement of the quartz is shown in Fig. 831. The right and left quartzes occupy alternate quadrants, so that opposite quadrants are of like kind; these opposite quadrants are cut from the same plate of right- or left-handed quartz of 3·75 millimetres thickness, which has been cut and polished perpendicular to the optic axis. The rectangular edge-strips of the four quadrants are carefully polished and cemented together so as to form a truly plane-parallel plate absolutely perpendicular to the axis. The lines of junction are just visible, appearing like a pair of cross-wires, the purposes of which they admirably serve. When the Nicols are parallel, therefore, the transition violet tint afforded by a plate of quartz 3·75 mm. thick is produced, the whole field being evenly lighted and coloured, crossed by the rectangular fine black lines of division of the quadrants. The least rotation of the Nicol, however, in either direction, or the introduction of a crystal-plate into the optical train, on the stage of the microscope, upsets the colour balance, unless the extinction directions of the crystal happen to be parallel to the vibration planes of the Nicols, and introduces red in one pair of opposite quadrants and blue in the other pair. Or if the Nicols be crossed, an even yellow tint is shown, which on the slightest rotation of the analyser or the introduction of a crystal-plate, obliquely as regards its extinction directions compared with the planes of the crossed Nicols, passes into brilliant colours corresponding to opposite directions in the spectrum, a bright orange being produced in one set of quadrants and a deep bluish green in the other. The usual mode of use is to have the Nicols crossed, to place the corner of one of the quadrants, that is, the centre of the plate, to a corner of the crystal formed by the intersection of two edges, and one of the lines to one of the edges, to be used as the edge of reference; and then to rotate either the Nicols and eyepiece together in the manner of the Dick microscope, the crystal being fixed on the stage, or to rotate the crystal, the Nicols and eyepiece being fixed, until the even tint is again restored. The angle between the two positions, as measured in the two respective cases on the circle *n* of Fig. 824 or *a* of Fig. 825, or on the rotating stage circle *p* of Fig. 821, will be the desired extinction angle of the crystal-plate. This eyepiece is also useful with high powers for detecting double refraction and determining its sign in minute crystal fragments.

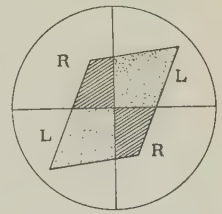


FIG. 831.—Effect of Introduction of Crystal on Even Field of Bertrand Quartz Plate.

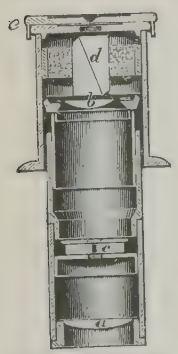


FIG. 832.—Calderon Double-calcite-plate Eyepiece.

The Calderon Double-calcite-plate Eyepiece.—A special eyepiece fitted with a Calderon stauroscopic double plate of calcite similar to that employed in the von Groth stauroscope shown in Fig. 723 on p. 975 may, however, be employed equally well in stauroscopic determinations of extinction with the microscope. Such an eyepiece is shown in Fig. 832, and it includes a special analysing Nicol, which is not essential, however, the hinged ordinary analysing Nicol of the Dick microscope serving equally well, provided the eye-aperture is similarly restricted by a cap with small hole. The eyepiece is of the negative Huyghenian type, *a* and *b* being the two plano-convex lenses. The Calderon double plate of calcite *c* is of similar construction to that of the stauroscope described in Chapter XLV. (p. 976), and is enclosed between two diaphragms with somewhat small apertures, which afford the convenient amount of field and the upper one of which is focussed by the adjustable eye-lens *b*; the line of demarcation (trace of plane of cementation) between the two halves of the calcite plate (exaggerated in thickness in Fig. 832) forms the vertical diameter of the circular field. The analysing

Nicol *d* is rotatable in the usual manner and carries a divided bevelled circle, rotating over a vernier-flange at the top of an outer tube not shown in the figure, which fits directly in the upper end of the optical tube of the microscope. Above the Nicol is fitted the cap *e* with very small circular aperture, which is absolutely necessary in order that the observations of extinction may be made for the precise direction of the microscope axis.

The Projection Eyepiece.—The large microscope of the Dick pattern now described, with an unusually large polarising Nicol such as has been fitted to the author's instrument, and an especially large analysing Nicol (the outer carrying tube of which is almost exactly like that of the direct-vision spectroscope shown in Fig. 840 on page 1167) which is given with the instrument to fit directly over the eyepiece and replace the one at *l* in Fig. 821 (which latter can be thrown back on its hinge out of the way), serves admirably for projection purposes, and particularly for the photography of interference figures round the optic axes of crystals in convergent light. But for this object a special "projection eyepiece," one of a pair magnifying respectively three and six diameters, is advisable. This eyepiece is specially corrected to give a flat field on the screen or photographic plate. Such a projection eyepiece is shown in Fig. 833. The eye-lens, in this case the projecting lens, is a specially calculated achromatic combination of two lenses, which serves its purpose admirably. The draw tube containing it is furnished with a cap adapted for attachment to it of the large Nicol analyser; and it is provided with a spiral adjustment for the amount of its withdrawal out of the main tube, for accurately focussing a diaphragm in the latter on the screen or sensitive plate; the flat surface of the annulus closing the main tube is graduated to afford, with the aid of an indicator mark on the cap, a record of the proper adjustment for a given screen distance.

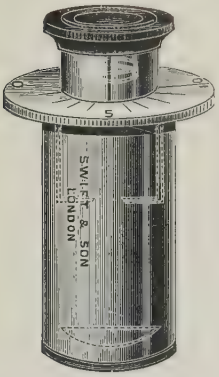


FIG. 833.
Projection Eyepiece.

With the aid of these projecting eyepieces, fitted to the Dick microscope here described, the interference figures in convergent polarised light given in this book have been directly photographed, some in white light and others in monochromatic light produced by the spectroscopic monochromatic illuminator described in Chapter XLIV., employing the electric arc as source of light; a Wratten and Wainwright K yellow screen was sometimes used in the case of the white-light figures, held in the free aperture of the slider π (Fig. 821), and either Wratten and Wainwright panchromatic or improved drop-shutter plates or Sanger-Shepherd B plates, and a Watson premier half-plate camera, were employed.

The Universal Stage of Fedorov for the Investigation of Microscopic Crystals.—The methods of Fedorov,[1] to which further reference will be made in the next chapter, depend on the use of an ingenious little stage apparatus, which is to the Miers stage goniometer what the three-circle goniometer is to the ordinary single-circle goniometer. It permits not only the usual rotation of the microscope stage, but also affords rotation about four other axes. In its latest form, including two additional circular arcs due to F. E. Wright,[2] it is shown in Fig. 834, no less than four divided circles being provided.

[1] *Zeitschrift für Kryst.*, 1893, *21*, 574; 1894, *22*, 229; 1896, *25*, 113 and 351; 1896, *26*, 225; 1897, *27*, 337; 1898, *29*, 604.
[2] *American Journal of Science*, 1907, *24*, 343.

The whole apparatus is carried by a stage-plate *a* with wide central aperture, which can be clamped to the fixed stage of the microscope by the screws *b*. From this stage-plate rise vertical brackets *c*, for the support in suitable bearings of the main horizontal goniometer-axis. Rotation of the milled head *d* to the left brings about rotation of this axis and of the vertical goniometer-circle V_1 carried directly and rigidly by it, and of the whole of the other circles carried indirectly about this horizontal goniometer-axis, which latter may be conveniently distinguished as axis 1 and is lettered correspondingly A_1. The screw *e* serves to fix this axis at any position of the circle V_1, as indicated by the vernier *f*. The second circle H_1, which may be used as a horizontal ordinary rotating stage-circle if desired, is carried by the goniometer-axis A_1, which thus forms a diameter; but the circle itself is rotatable—either by hand by means of its milled periphery, or by a little milled-headed driving winch (not shown in the figure), which can be thrown out of gear by a spring when not required—in its own plane, its position being indicated by a vernier *g*, and fixation in any position being possible with the aid of the clamping screw *h*; the axis A_2 of this second circle H_1 is consequently at right angles to the goniometer-axis A_1, and may thus be called axis 2. The plane of this ring-circle H_1 obviously rotates with V_1, while H_1 also rotates in its own plane.

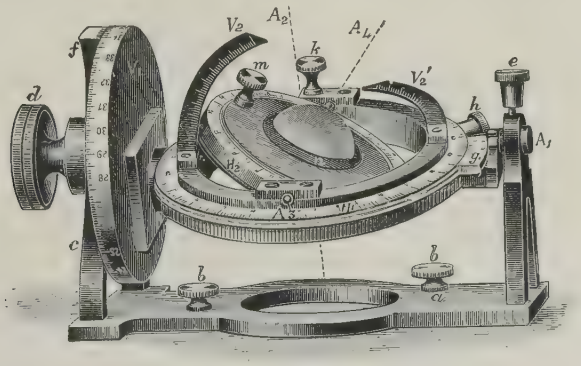


FIG. 834.—The Universal Microscope Stage of Fedorov.

Within this in gimbal manner a second ring H_2 is swung, on an axle A_3, which may be termed axis 3, lying in the plane of H_1, and capable of fixation by the clamping screw *k*. Its altitude with respect to H_1 can be measured by a graduated arc V_2 or a similar one V'_2 on the other side, both being hinged so that the one not required can be turned down out of the way. Within this circle H_2 and in its plane a glass stage *l* is capable of rotation, the position being indicated by another vernier just hidden underneath out of sight, and fixation secured when desired by the screw *m*. The axis of rotation A_4 of this innermost disc may be called axis 4. In a metallic annulus *n* in the centre of this glass stage there fits a circular glass plate with truly plane and parallel polished surfaces, on which the crystal under investigation is simply laid when it is to be examined in parallel polarised light. When convergent light is to be used, for the measurement of the optic axial angle, a glass hemisphere *o* is laid over the minute tabular crystal or larger crystal section-plate as shown in Fig. 834, with a drop of a highly refractive liquid—cedar oil or glycerine being very suitable—to form a uniting film between the glass plate and hemisphere, and in which the crystal is immersed. A similar hemisphere is fitted with its liquid film also beneath the glass plate, the two hemispheres thus together forming an optic-axial-angle apparatus on the principle of the method of Adams, which, while generally now discarded for the ordinary measurement of good-sized crystals, has found its real utility in microscopic optic-axial-angle

goniometry. Two brass annuli, at the ends of pivoted or hinged arms and fitted with locking screws, serve to secure the two hemispheres in position.

Klein's Universal Stage Rotation Apparatus. — This is another very useful little stage apparatus, especially for the investigation of a small crystal in a cell of liquid the refractive index of which is approximately the same as the mean of the three indices of the crystal for sodium light. It is shown to the left in Fig. 835, as constructed by the firm of Steeg & Reuter. It enables measured rotations to be effected about three rectangular axes, the movements being of a similar nature to those of the ordinary goniometer, with the addition that the two circular adjusting segments movable in planes at right angles are graduated, as they are, in fact, in the case of the cutting-and-grinding goniometer described in Chapter XLIII. It can be used equally for the determination of the extinction angles in a zone of faces, in the search for the optic axes, and for the measurement of the approximately true

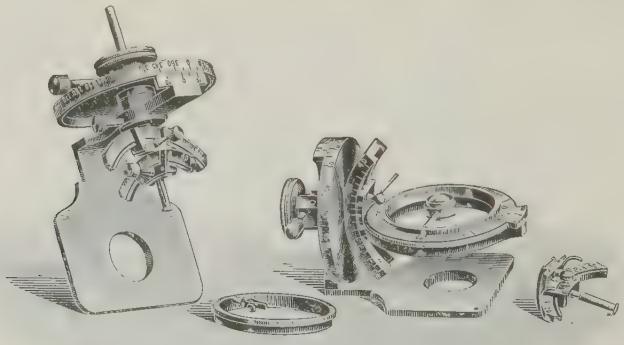


FIG. 835.—Universal Stage Apparatus of Klein.

angle $2V_a$ between the optic axes, in an immersion liquid of the same refractive index as the crystal. An additional holder, shown more to the right in the figure, carries, instead of the crystal directly, a couple of Adams hemispheres, between which the crystal is enclosed with a drop of the liquid, the liquid cell being discarded when this special fitting is used for the measurement of the optic axial angle.

The Compensator of Babinet.—For the determination of the difference between the two refractive indices corresponding to the vibration (extinction) directions of a crystal-plate, that is, for the determination of the amount of its double refraction, a special fitting essentially involving a double-wedge plate of quartz and known as a Babinet compensator is employed. It is placed under (behind) the Nicol prism analyser in any form of measuring polariscope, but is most conveniently used as a special positive eyepiece, carrying the quartz-plate compensator at its focal plane, on the crystallographic microscope. The analysing Nicol prism is then carried above the eyepiece.

The compensator of Babinet consists of two slender quartz wedges, shown very much thickened, diagrammatically, in Fig. 836, and in Fig. 837, above in general appearance and below in section, as constructed especially satisfactorily as an eyepiece for the microscope by the Société pour la Construction des Instruments de Physique à Genève.

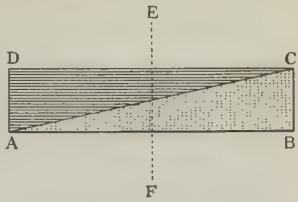


FIG. 836.—Babinet Compensator.

The wedge ABC is cut so that the optic axis of the quartz crystal is parallel to the edge of the wedge, which is perpendicular to the page in the figure, as indicated by dots in the shading, representing lines seen end on. The other wedge ACD is made of equal angle and so that the axis is perpendicular to the edge of the wedge and parallel to the face CD. Two such wedges laid together form a parallel plate, which under crossed Nicols in parallel light when arranged at 45° to the vibration directions of the Nicols shows a black band in the centre parallel to the edge of the wedge, and

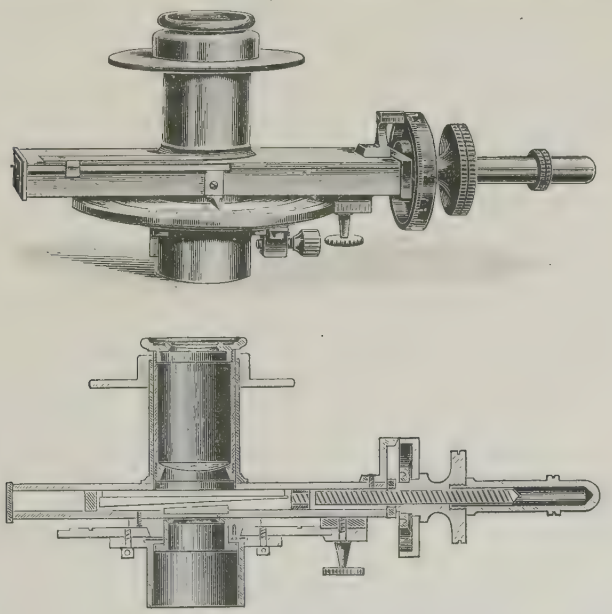


FIG. 837.—Babinet Compensator Eyepiece.

parallel spectrum bands on each side, separated by white interspaces and showing the usual sequence of Newton's orders. Fig. 838 is a direct photographic reproduction of the screen picture afforded by a large Babinet double wedge, when placed between crossed Nicols on the stage of the projection polariscope (Fig. 633, page 853). This effect in white light is very much the same as that shown in Fig. 807 (page 1104), Chapter L., as produced by the four-wedges biquartz, the only difference being that the bands are there produced by thicker wedges and by utilising the optical rotational property of quartz, whereas here it is the double refraction which is utilised. In monochromatic light Babinet's compensator shows equally spaced dark bands with luminous interspaces. When the Nicols are parallel and white light is used, a white band occupies the centre, and the colours of the other bands are complementary to

those exhibited when the Nicols are crossed. In monochromatic light, dark bands occupy the places where with crossed Nicols the bright interspace-bands occur.

The wedges are not cemented together, in the actual compensator, but are separated by a sufficient air layer to permit of the movement of one of them parallel to its base and in the direction of its length, by means of a micrometer screw furnished with a divided drum, the number of whole turns of which is also recorded by a scale on the rectangular micrometer box; in another form of the compensator, supplied to the author by Fuess for use with the large No. 1*a* spectrometer-goniometer, a divided numbering wheel, which turns one division for one whole revolution of the screw, replaces the scale. One of the quartz wedges is fixed, while the other, the upper one in Fig. 837, is mounted on a frame moved by the screw, so that the wedge which it carries is caused to move one way or the other over the fixed wedge. Just below the quartz a pair of parallel spider-lines are arranged, at the focus of the positive eyepiece, and the drum can be so set that its zero corresponds to the placing of the black band symmetrically between the two spider-lines, as shown in Fig. 891 in Chapter LVII., in the case of other interference bands. When the zero of the drum is thus arranged to correspond to the adjustment of the black band, the indicator of the scale or wheel should also be opposite a division mark. The whole compensator is rotatable about the axis of the microscope; it can readily, therefore, be placed so that the directions of vibration of the quartz are at 45° to those of the Nicols.

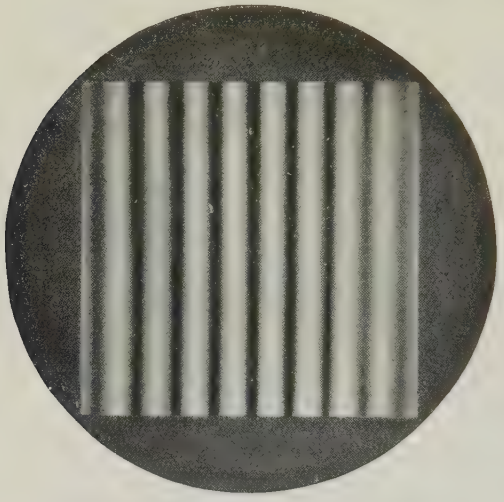


FIG. 838.—Interference Bands produced by Babinet Double Wedge between Crossed Nicols.

When thus arranged at 45° with the crossed Nicols the dark band seen in white light, in the centre of the parallel coloured bands, corresponds to the trace of the plane of equal thickness, EF in Fig. 836, of the two wedges, where compensation is complete for all rays and the dark field of the Nicols prevails unaffected as the net result. For plane-polarised light falling on either face of the composite quartz plate at 45° is separated into two rays vibrating respectively parallel and perpendicularly to the optic axis, that is, to the horizontal rectangular edges of the plate. On entering the second wedge the directions of vibration are retained but the velocities are interchanged, the ray which travels the faster in the first wedge travelling the slower in the second. Hence, if the thicknesses are equal there is no relative retardation of one ray behind the other, the sum of the two velocities for each ray being the same. As we recede from the centre, however, or as we move the line of equal thickness (as we do in the compensator), differences of phase will more and more manifest themselves, and wherever the

difference amounts to a whole wave-length from the equality conditions of the central line there will be another dark band in homogeneous light, or a spectrum band in white light owing to the distances from the centre for the extinction of light of particular wave-lengths being different. When the Nicols are parallel the black bands in monochromatic light occupy the points corresponding to $\lambda/2$, $3\lambda/2$, $5\lambda/2$ and so on. That is, with Nicols crossed black bands occur at intervals corresponding to even multiples of the half wave-length, and with Nicols parallel to odd multiples of the half wave-length.

The Fuess Microscope.—The Dick method of simultaneously rotating the Nicols has now been adopted by Fuess in the more recently constructed and truly excellent models supplied by the firm. The fine instrument shown in Fig. 839 was constructed by Fuess for J. Hirschwald.[1] It has the novelty of a second inner body-tube, which is rotatable and carries with it the eyepiece *a* (which is shown separately to the left in Fig. 839, as the main figure shows the Abbe camera lucida in position covering the eyepiece, as described in the next section), the analysing Nicol *b* which is mounted in the old place just above the objective, in order to avoid restricting the field, and the Bertrand lens *c*; the polarising Nicol *d* also rotates simultaneously with it, the rotation being effected either by the large toothed wheel *e* which rotates a smaller one *f* attached to the shaft *g*, or by the similar large wheel *h* at the lower end of the shaft and which carries the polarising Nicol. Sometimes it is inconvenient to rotate the eyepiece, and in this case it can be locked to the outer body-tube by the arrangement shown at *i*. When unpolarised light is desired, the analysing Nicol *b* can be pushed out of the two body-tubes by means of a spring handle *j*. Also, the polariser may be kept stationary, while the analyser and eyepiece with its cross-wires rotate, or the polariser and the eyepiece may both be maintained stationary while the analyser alone rotates. The eyepieces employed on this instrument afford a much larger field than the older ones supplied by Fuess, so that equal results may be obtained with lower-power objectives, and with very little loss of definition. The Bertrand lens can, of course, be pushed out of both tubes when convergent light is not required. A further novelty on this microscope is an electric glow-lamp mounted above and to one side of the stage in a small tube *k* closed by a condensing lens, in order to effect the illumination of opaque crystals from above; it is held in such a manner by the fitting *l* as to be readily directed in the most favourable manner for attaining the illumination desired.

The Becke Drawing Table and Abbe Camera Lucida.—For the microscopic investigation of crystals by the methods which have been described and recommended by F. Becke[2] a camera lucida and drawing table are required, and in the form in which these further accessories are constructed by Zeiss they are also shown in Fig. 839, as combined with the Fuess crystallographic microscope just described. The method

[1] *Centralblatt für Mineral.*, 1904, *20*, 626.

[2] Tschermak's *Min. petr. Mittheil.*, 1894, *14*, 563; 1896, *16*, 180; 1905, *24*, 35

of Becke consists essentially in preparing a graphical representation on a stereographic projection of the optical phenomena observed with a crystal-plate, as will be more fully described in the next chapter. By means of an Abbe camera lucida the interference figure in convergent

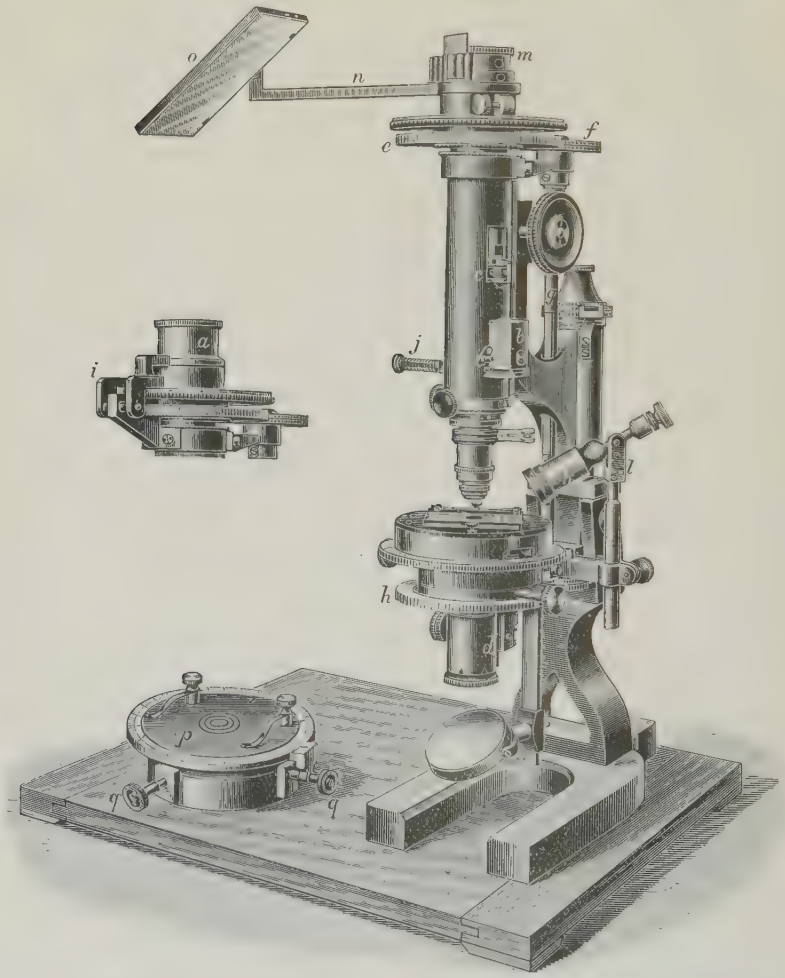


FIG. 839.—The Fuess Crystallographic Microscope, with latest improvements by Hirschwald, and the Abbe Camera Lucida and Becke Drawing Table in Position.

polarised light is rendered simultaneously visible with the drawing paper laid on a small rotatable drawing table, arranged on the large base-board on which the microscope is mounted ; this drawing table can be accurately centred by means of three screws placed at intervals of 120°, or two screws at 90°. The rotating plate of the drawing table has a series of concentric circles engraved on it, in order to facilitate rapid centring and

to obtain identity of the axis of rotation with the centre of the image of the interference figure.

The camera lucida *m* is fitted over the eyepiece *a*, and is connected by means of a supporting arm *n* with an adjustable mirror *o*, which reflects the light rays from the drawing table *p* to the camera lucida, the phenomena visible to the eye looking down the microscope being thus as it were projected on the image of the drawing paper, and the pencil point held on the latter will also be in focus at the same time. An accurate drawing of the appearance of the interference figure can then be made. Such records enable geometrical constructions to be made and graphical methods of calculation to be employed, which result in approximate determinations of the optic axial angle and other optical constants being arrived at in cases which would otherwise be hopeless.

The Abbe camera lucida has the advantage of focussing both the drawing and the pencil equally, even under considerable magnification. The optical part consists of the "Abbe cube," composed of two equal totally reflecting rectangular and 45° glass prisms, cemented together and placed at the eye position above the eyepiece. The cemented surface of the upper prism is silvered, except within a central circle of two millimetres diameter, through which the rays from the field of the microscope emerge to the eye looking through. At the same time the drawing table is reflected in the silvered mirror, together with the pencil in the observer's hand when drawing. The brightness of the image can be modified by a smoked glass, a small rack for three such smoked-glass plates being provided. The accuracy of the method depends on the faithfulness of the drawing, the precision with which the drawing is centred by the screws *q*, and the care with which measurements are subsequently made on the finished drawing.

Spectroscope for Use with the Microscope.—An efficient yet very simple direct-vision spectroscope is furnished with the Dick microscope by Messrs. Swift, for the study of the absorption bands of crystals under the microscope. It consists of two parts, shown in Figs. 840 and 841. The first part (Fig. 840) is the direct-vision spectroscope itself, which is attached over the eyepiece, the large analysing Nicol prism referred to on page 1160 being fitted over it if desired. The second part (Fig. 841) consists of an adjustable slit, which fits as a slider in the slot

FIG. 840.—Direct-vision Spectroscopic Attachment.

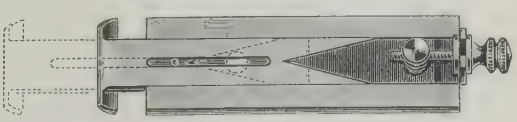


FIG. 841.—Adjustable Slit of Spectroscopic Attachment.

(*w* in Fig. 821) cut in the eyepiece tube. The construction will be obvious from the figure. Even crystals affording but relatively faint bands can readily be studied as regards their light absorption with the aid of this spectroscopic eyepiece fitting.

Bausch & Lomb Research Microscope. — A description of a petrographic microscope constructed for research purposes by the Bausch & Lomb Optical Co., Rochester, N.Y., has been given by F. E. Wright to the Optical Society of America.[1] The distinctive features are the following: a large Ahrens polarising prism; a sensitive-tint plate mounted in a sliding carriage revolvable about the axis; an aplanatic condenser, numerical aperture 1·4; a sub-stage apertometer; a rigid bar connection for the simultaneous rotation of the two Nicols; a sliding adjustable mount for two objectives, so adjusted that if one objective is in focus and centred, the second on insertion is also automatically focussed and centred; a combination wedge; negative and positive lenses below and above the polariser for the correction of astigmatism; a swing-out lens above the Bertrand lens to ensure the formation of an image of the object plane in the plane of the iris diaphragm in the draw-tube; a universal eyepiece with one-tenth millimetre co-ordinate scale, graduated quartz compensator, and biquartz wedge plate; a small prism mounted in a slider below the eyepiece for observation of interference figures by the method of Lasaulx; and a sliding diaphragm with eyepiece for observation of interference figures of small mineral-crystal grains. With this microscope it is claimed to be possible to measure the optical properties of minute crystal grains and plates in thin sections with a degree of accuracy hitherto attainable only with much larger grains and plates, and in much less time. Refractive indices can be ascertained in grains only a few microns thick, and the double refraction and optic axial angles on grains only 0·01 millimetre in diameter, although of course larger ones are preferable if obtainable. The fine adjustment screw, moreover, reads to 0·001 millimetre, without any backlash. The instrument is specially suitable for use in connection with many of the special methods of research with very small crystals, and especially with those contained in rock-sections, which are described in the next chapter.

The Microsclerometer.—Reference has already been made in the chapter on Hardness (p. 539) to the elaborate instrument devised by T. A. Jaggar,[2] which he terms the microsclerometer. It is designed for the determination under the microscope of the hardness of crystals which may either be ordinary small individuals or section-plates of such, or those contained in the thin sections of rocks. Indeed, any crystal or plate not too large to be dealt with on a microscope stage is suitable, and the surface investigated may be either that of a natural face or that of a ground and polished section-plate. The essential principle is that a diamond point is rotated at a uniform rate on the orientated crystal face or section-plate, under a uniform load, and to a uniform depth of abrasion or penetration. The number of rotations varies as the resistance of the material to abrasion by diamond, and is a measure of the duration of the abrasion. The instrument is shown in Fig. 841*a* above in plan, and below in elevation.

It consists of a balance beam with a rotatory diamond carried below one end, clockwork apparatus for rotating the diamond at a uniform

[1] *Journ. Optical Soc.*, America, 1917, *1*, 15.
[2] *Amer. Jour. of Science*, 1897, *4*, 399.

rate, apparatus for recording the number of its revolutions, and for recording the depth of its penetration into the crystal. The whole is

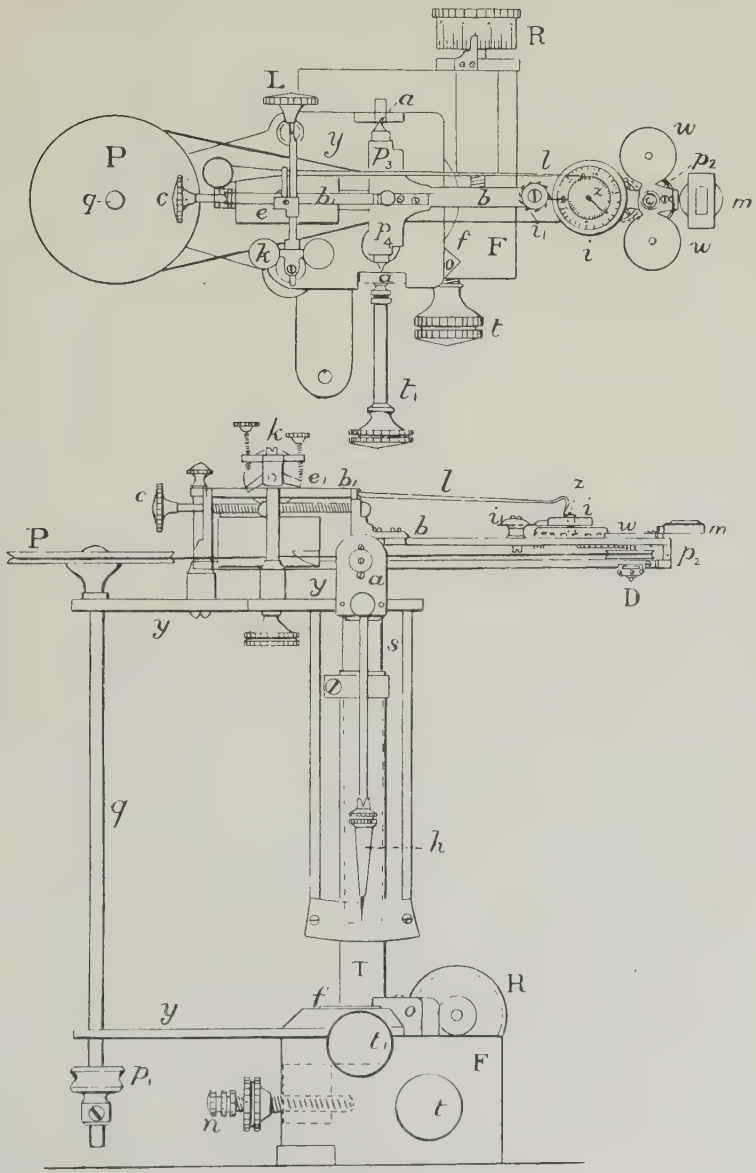


FIG. 841*a*.—The Microsclerometer.

mounted on a stand, fitting in an adjustable and rigidly fixable manner into the fork of the microscope stand. The main bulk of the apparatus

is carried by the outer rotatable cylinder of the column T with flanged base *f* rising from the block F, the amount of rotation being measured by the screw with graduated head R. The screws *t*, *t'*, and *n* enable fixation of the whole stand to be effected in the desired position. The rotating gear, the pulleys P and p_1, their axle *q* and yoke *y*, for the diamond D is supported below by an extension of the foot-plate-flange *f*, and above in a manner which will be clear from the figure. The balance beam *b* is double, pivoted at *a*, and counterpoised by a weight adjustable by the screw *c*; the smaller pulley p_2 of the diamond-rotating gear is accommodated between the two bars of the beam. The indicating pointer of the beam carries also a counterpoise *h* for all the upper gear.

The diamond D is a cleavage tetrahedron with a perfect point. The cleavage tetrahedron may be obtained in duplicate in great perfection among the "cleavings" used for making diamond cutters and pencils, and such tetrahedra are specially valued for their sharp points; as each has four points it is not difficult to find a point of perfect form from among a very few specimens. The points should be turned upwards successively under the microscope, and examined with a high power, until one is found which shows the three edges converging to a sharp point to the uttermost focussing power of the microscope. The selected one is centred rigidly in its brass mount by first soldering it in, and afterwards trimming the metal around it on the jeweller's lathe, leaving the right amount of diamond exposed. The mount in turn is fixed in a chuck, by three radial screws, carried at the lower end of the pulley axle, so that the diamond projects downwards below the end of the balance beam. The little pulley p_2 is connected with the driving pulley P by a silk band, and to prevent the tension of the band from interfering with the balance beam two small pulleys p_3 and p_4 rotating in the pivot axis are added, the two portions of the band being parallel between these pulleys and p_2. Two weighting pans *w* are carried, one on each side, for the definite loading of the beam end and diamond, leaving room between them for the microscope objective to be focussed down on to the Zeiss micrometer scale on glass *m*, carried at the extreme end of the beam. The rotations are recorded by the parts lettered *i*, *z*, and *l*. The driving is best effected by ordinary clockwork, so as to ensure uniformity of rate. The balance and recording apparatus can be simultaneously locked by a half-revolution of the screw L, the adjustment screws *k* assisting to determine the locking position; the rotation of L causes an excentric *e* to press upon both the beam-bar *b* and the spring-lever *l* which controls the indicator *i*.

It is arranged that the micrometer scale *m* is visible in the field of the microscope at exactly 10 mm. from the axis of rotation of the diamond point D, and that this is one-sixth of the distance of the latter from the balance beam pivot *a*. Hence, if the microscope be focussed on the micrometer before and after the boring with the diamond, the depth measured by the fine adjustment screw of the microscope will be seven-sixths of the actual depth bored. Rotation of *m* is then effected until the scale stands at right angles to the beam, and then tilted slightly

until under a high power only one graduation mark at a time is visible, and that a distance of 0·01 mm. of downwards or upwards focussing is necessary to bring each successive line into focus. Then as the diamond bores, it can be followed and the depth of boring thus measured.

In making a determination the crystal face or plate is fixed on the stage and viewed by the microscope under a low power, and the place selected for attack by the diamond is centred. It is then moved along 10 mm., so as to be exactly under the diamond when the latter is brought into position, when the lock L is released, and the diamond allowed to rest on the crystal, while the micrometer *m*, at its tilt for 0·01 mm. intervals, is focussed under a high power, so that the lower of two lines near the centre of the field is in focus. L is first locked while the rotation is started with the clockwork at a uniform speed ; L is then unlocked and the boring commenced. The uniformity of the rate is indicated by the movement of the index hand of *i*, the initial position and number of revolutions of which must be recorded. The micrometer focus is also watched under the microscope, and when the next upper micrometer line appears sharp, and the depth of boring is consequently 0·01 mm., the lock is closed and the clockwork stopped.

The action of the diamond is slow, and there is a rapid increment of resistance with increased depth, owing to the increase of the surface of abrasion. With a weight of 10 grammes and a rate of 10 revolutions per second, it required 3000 revolutions to penetrate to a depth of 0·01 mm. in an ordinary cover glass, the test thus occupying 5 minutes. A weight of 10 grammes is a fairly average useful one ; it is too little for the minerals much harder than glass, but too much for the softer substances. Hence, a somewhat greater weight is convenient in the former case, and a less one in the latter case.

Microscope for Higher Temperature Work and for the Study of Liquid Crystals.—This chapter on the crystallographic microscope may well close with a brief description of an instrument specially adapted for microscopic work on crystals at higher temperatures. It is shown in Fig. 842, and is constructed by Messrs. Steeg & Reuter of Homburg ; it is particularly suitable for the study of the remarkable liquids which afford the phenomena of "liquid crystals," which have been so ably studied by Lehmann, and an account of which will be given in Chapter LX.

The whole instrument and its heating and cooling arrangements are designed to effect changes of temperature as rapidly as possible consistent with safety. Every precaution is also taken to protect the optical and finely constructed parts from the heat and from condensing vapours. Hence, it is possible with the instrument to continue the study of the phenomena up to a low red heat. There are two object stages, the lower completely covered one being divided into single degrees, and rotatable. The upper one may be rotated with or independently of the lower, and is removable to facilitate thorough cleansing after the operations. There are provided two blow-pipe gas jets, two cooling air jets, one for slow and the other for rapid cooling, together with the necessary gas and blow-pipe connections provided with

finely adjustable taps. Between the polarising prism and the stage a capillary-tube ring of miniature gas jets can be inserted, and the rise of temperature may be effected either with great slowness or very rapidly, as desired. The usual fittings, such as an analysing Nicol, Bertrand lens, convergent light condenser, all readily detachable together with a coarse and a fine adjustment, are all given on this useful microscope, with which most of the experiments described by Lehmann may be repeated.

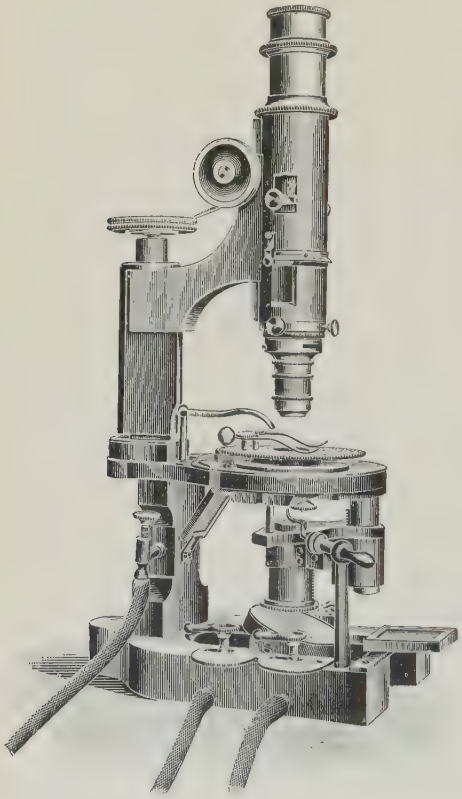


FIG. 842.—Steeg & Reuter Microscope for the Study of Crystals at Higher Temperatures.

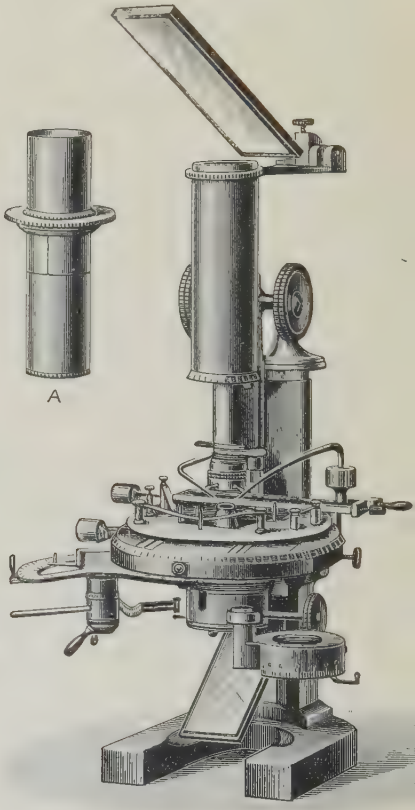


FIG. 843.—Zeiss Microscope for Higher Temperature Work.

A very efficient microscope for higher temperature work, especially suitable not only for the study but for the projection of the phenomena of the so-called "liquid crystals," has also been perfected by Zeiss. Its latest form is represented in Fig. 843, as arranged for projection experiments, the eyepiece shown separately to the left at A being replaced by an adjustable mirror for projecting the image of the microscope field on the screen. A detailed description of the instrument will be given in

Chapter LX. in connection with the discussion of the work and demonstration experiments of Lehmann.

Projections with the Microscope. — The Dick microscope, when supplied with larger polarising and analysing Nicols than usual and a set of projecting eyepieces, as in the case of the author's instrument, may be employed for screen projections of ordinary temperature crystallographic phenomena, when a disc not exceeding three feet in diameter is desired. It is also eminently suitable for photographic projection purposes, as already mentioned.

But screen projections on a larger scale with the polarising microscope, which have ever been difficult on account of the large amount of light lost by polarisation, may be very efficiently carried out with the form of projection polarising microscope shown in Fig. 844. It is very simple, yet the author, who has spent much time in investigating all the possible methods of screen projection of optical phenomena, and in personally testing all the apparatus yet introduced for the purpose, finds it more efficient than any other. A 6- to 8-feet disc may readily be obtained brilliantly illuminated, of crystals in polarised light, employing a Newton $1\frac{1}{2}$-inch projection objective; moreover, almost equally good results are obtained with the $\frac{4}{10}$ths-inch higher-power Newton projection objective. No eyepiece, but an adjustable sub-stage condenser also supplied by Messrs. Newton is used, to concentrate the parallel beam received from the polarising Nicol. The latter, with its parallelising concavo-convex lens at the lantern end, the lantern itself with its condenser and water-cell in front, are precisely as already described in Chapter XL. for projections in polarised light, but the second large analysing Nicol may be quite well replaced by a smaller Nicol, such as is shown at the extreme right in Fig. 844, in position after the objective; for the beam is very narrow as it leaves the objective. As a matter of fact there is practically nothing to choose between the screen effects produced with the large or the small analyser, so that whichever is most convenient at the moment can be used. The microscope fitting is simply arranged as an additional accessory on one of the adjustable stands sliding in the guiding-bed basal plinth or lathe-bed of the projection apparatus, the particular stand having a longer base (parallel to the bed) than the others except the Nicols, in order to secure rigidity. The stout carrying rod rising from within the hollow supporting column, in which it is adjustable for height by a fixing screw, terminates above in a horizontal tube with flanged head, the two forming a T-piece. The cylindrical bracket-column (arranged horizontally) of the microscope fits within this tube, and is secured to the flange by two milled-headed screws. The objective and analysing Nicol are carried by a second bracket, the column (also horizontal when in position as in Fig. 844) of which is of triangular section fitting and moving by rack and pinion in a similarly shaped boring in the fixed bracket-column just referred to, which carries the stage and sub-stage condenser. The objective may thus be racked to the proper focus in the usual manner, a circular metal plate being provided immediately after it to ward off from the screen any stray reflections from the illuminated object or

parts of the apparatus. The fitting of the small Nicol is hinged so as to enable it to be rotated out of the way when not required. The stage is rotatable and graduated, and the sub-stage condenser in its mount is adjustable in an outer tube to the most efficient position found by experiment to give the best results on the screen. With the ready means afforded by the adjusting table of the lantern lamp for centring the electric arc, and for adjusting its distance from the condenser, every desirable adjustment of the illumination is provided for.

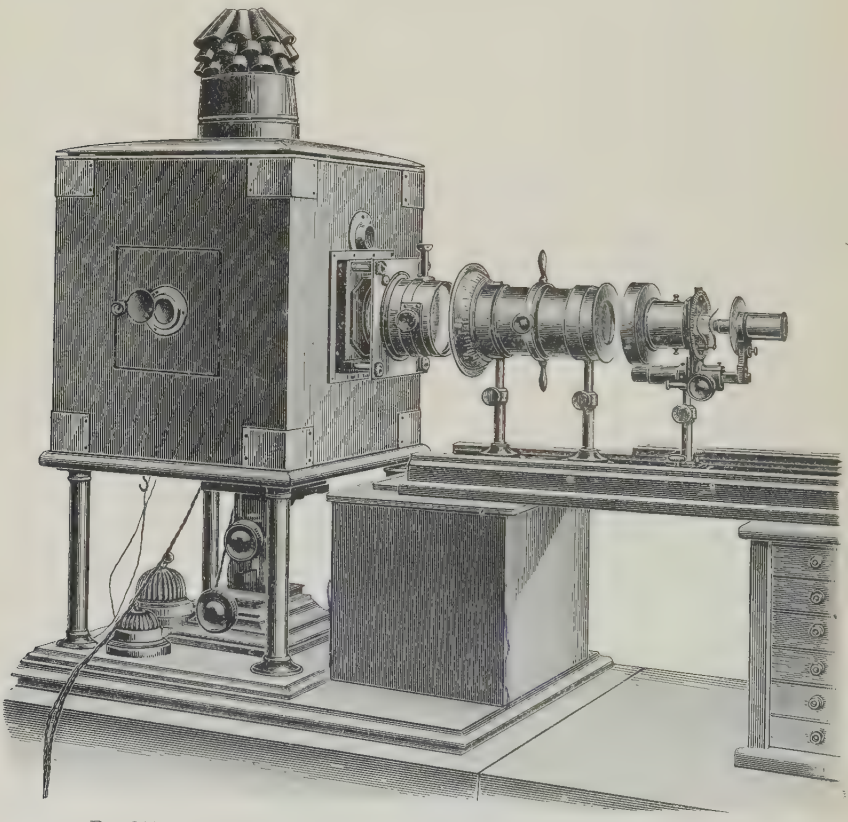


FIG. 844.—Arrangement for Screen Projection with the Polarising Microscope.

The above microscope fitting may be also attached directly (by means of the wide cap which forms the left extremity of the sub-stage condenser tube) to the front of the water-cell when it is not desired to employ polarised light, but for crystallographic purposes this latter is usually desirable and necessary, so that the arrangement shown in Fig. 844 is the most convenient one. It has the further advantage, besides being simple and involving few lenses with the corresponding few occasions for loss of light by reflection, of keeping remarkably cool, being sufficiently far

removed from the lantern, and being unenclosed in restricting and unventilated tubes.

Provision is also made for use of the fitting vertically upright, for experiments involving the direct projection of crystallisations from solutions. The stout columnar supporting rod (shown in Fig. 844) which passes down into the hollow column of the stand is replaced for vertical work by a longer column, and the tube and flange for the reception and fixation of the microscope bracket-column form a vertical rigid continuation of the column itself. The fitting is thus raised also sufficiently high to enable an adjustable mirror to be fitted to the column at the height of the polarising Nicol. The parallel beam of light is reflected by the mirror vertically upwards through the sub-stage condenser and microscope, and the light rays issuing upwards from the latter are projected to the screen by means of an adjustable totally reflecting rectangular prism, which is suspended by a bracket just over the polariser. Some loss of light is always inevitable in vertical reflected projection, but the results are still adequate as regards illumination with a 6-feet disc, and very brilliant with a 5-feet disc.

The Zeiss heating microscope shown in Fig. 843 may very conveniently be used with the electric lantern disposed as in Fig. 844, for the projection of " liquid crystals " or other experiments with crystals at higher temperatures. The water-cell is left in position on the lantern front, but the large Nicol and the author's projection microscope are removed and the Zeiss microscope substituted, raised on a rigid stand to the right height above the plinth bed. The concavo-convex parallelising lens is detached from the end of the large Nicol, and separately carried on one of the adjustable stands, in order that a parallel beam of light from the lantern may be directed to the mirror at the foot of the microscope. The light is thence reflected upwards through the microscope to the mirror at the top of the latter, which is rotated and inclined to the right position which enables it to direct the rays to the screen.

CHAPTER LIII

OBSERVATIONS AND MEASUREMENTS WITH THE CRYSTALLOGRAPHIC MICROSCOPE

A GREAT deal of attention has lately been given to the determination of the characters of minute crystals, with the view of rendering the results more than merely approximate and more comparable with those obtained with crystals of larger size on the first-class measuring instruments described in the foregoing pages. The work of F. Becke, Fedorov, Klein, and F. E. Wright stands out prominently in this domain, all of whom have devised microscope details or stage instruments, and the two first mentioned of whom have elaborated original methods of attack, which enable the optical constants of minute crystals or crystal fragments to be determined with a remarkable degree of accuracy, considering the difficulty of the undertaking. The stage goniometer of Miers and the other useful fittings which, as well as the stage and other accessories just referred to, have been described in the previous chapter, together place at the disposal of the crystallographic investigator methods of far greater accuracy than formerly, and no investigation need be abandoned because of the minuteness of the crystals available.

Measurement of Crystal Angles with the Microscope.—The Miers stage goniometer may be employed for the measurement of the angles of microscopic crystals by the " illuminated-face " method or " Schimmermethode " of Brögger. The rays from a small collimating lens, with a bright spot or slit as source of light at its focus, are directed on the miniature crystal adjusted on the wax at the needle end of the axis of the stage goniometer, and the zone of faces to be measured is adjusted till the maximum brilliancy of illumination of each face is observed on rotation of the crystal axis of the goniometer. The angular position of each face is then determined by rotating the circle with the crystal till the face becomes just bright. It is then rotated further until the illumination of the face just disappears. Two or three further approaches are then made to these two positions, from the two respective sides. The mean of an equal number of readings for these positions on the two sides of maximum illumination will then give a very fair approximate value for the position of the face, when the latter, although minute, is good.

Another interesting and more accurate method of measuring crystal

angles under the microscope has been devised by Fedorov, for use with his universal stage (Fig. 834, page 1161), but which is equally applicable for use with the Miers stage goniometer. A black cross is marked on the under surface of the microscope objective to be employed, and light is reflected down the microscope axis from a lamp placed to one side, by means of a glass plate, of the character of the Gauss ocular or the Becker fitting described on page 41 and illustrated in Fig. 24. When the crystal is adjusted, on a special crystal-holder which replaces the central glass hemisphere of the stage, with a face perpendicular to the microscope axis, and is clearly focussed, the cross is invisible ; but on lowering the microscope so as to halve the distance between the crystal face and the objective—which is accurately possible with the aid of the scale (shown in Fig. 824) on the guide of the slider of the body-tube worked by the coarse adjustment, or if a higher power is being used by means of the graduated head-wheel of the fine adjustment—the cross becomes visible by reflection from the face, and can be used as a signal and placed to the cross-wires. The crystal is then rotated until the next face of the zone adjusted affords a similar reflection, and this also is placed to the cross-wires, the angle of rotation being measured on the goniometer vertical circle V_1 in Fig. 834, representing the universal stage, or the circle of the Miers stage goniometer, in the usual manner. The Fedorov universal stage may be regarded as a three-circle goniometer applied to the microscope, while the Miers stage goniometer is the ordinary single-circle goniometer similarly adapted for microscopic measurement. Owing to the difficulty of resetting a minute crystal on the needle-holder of the latter, and the obvious advantage of reducing the number of such settings, required for the measurement of a number of zones, the universal stage has here a considerable advantage, however.

The goniometer eyepiece shown in Fig. 829 may also be used to measure the crystal angles in any zone of faces on a tabular crystal so small as to be best investigated under the microscope, when the faces in question are perpendicular to the tabular plane. The method has been adequately described on page 1158 of the last chapter.

The Determination of Refractive Indices with the Microscope—(*a*) **Methods of the Duc de Chaulnes and of Sorby.**—The mean refractive index of a birefracting crystal, or the absolute refractive index of a cubic crystal, can be determined under the microscope by the method of the Duc de Chaulnes. This depends on the fact that the focus of a microscope alters when a transparent plate with truly plane and parallel surfaces is introduced between the objective and the object focussed. The amount of the change d is connected with the thickness t of the plate, and with the refractive index μ of the substance of which the plate is composed, by the formula :

$$\mu = \frac{t}{t-d}.$$

Let *a b c d* in the first drawing (*a*) of Fig. 845 represent such a plate, and F be the focus of the microscope when the plate is absent. When

the plate intervenes the rays from the focus F appear to come from the point F′, and the microscope has to be withdrawn by the amount FF′. The case before us is where F lies on or in contact with the lower surface of the plate. The apparent thickness t' of the plate, where $t' = t - d$, is the quantity experimentally determined by focussing first the upper surface—utilising surface polishing marks or dust particles, or better still marks silvered on the plate, as objects to be focussed—and then the lower surface as seen through the plate ; the real thickness t of the plate is also measured either before or afterwards with the aid of a thickness measurer, such as that described in Chapter LVII. and illustrated in Fig. 893, or else with the microscope itself used as a thickness measurer. In the latter case the ordinary microscope stage is covered by a thick slab of truly parallel glass, bearing a scratch or other defining mark such as a little engraved ring in the centre, as reference mark to be focussed. The plate of the crystal is then laid on this glass slab, taking care to exclude air by sliding

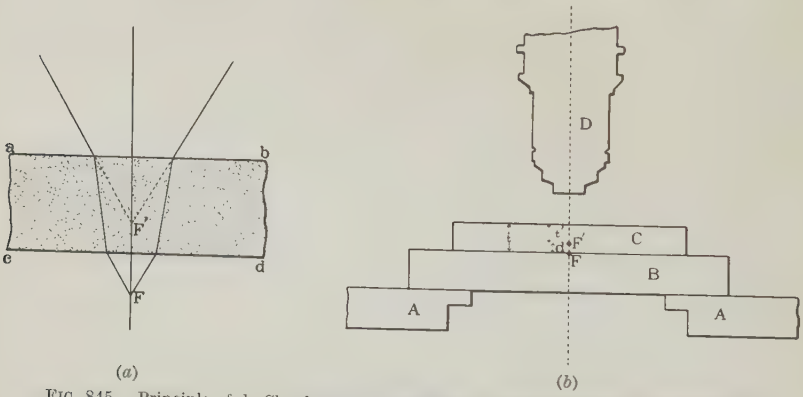


FIG. 845.—Principle of de Chaulnes, and Conditions in the Microscopic Determination of Refractive Index.

the crystal-plate on, and its upper surface is then focussed by its polishing scratches or natural markings. The fine adjustment is employed in moving the microscope between the two focussed positions, and the difference of the readings of the divided head and the total number of its whole revolutions afford the required thickness. When the crystal-plate is thicker than the extent of the fine adjustment movement the scale of the coarse adjustment can also be requisitioned, but usually this will be unnecessary. Now it can be proved that $t = \mu t'$. Hence, $\mu = t/t'$.

In the actual determination, when accurate results and not a mere approximate value are desired, a fairly high power requires to be used, not lower than a $\frac{2}{3}$rds-inch ; and the plate must not be too thick to permit of the lower surface being focussed by such a power. The excellent fine adjustment of the Dick microscope, reading to the thousandth of a millimetre, is particularly convenient and suitable for the measurement under these circumstances. The conditions are clearly

exhibited at (*b*) in Fig. 845. A reading is first taken for the focus of the reference mark F on the basal slab B, laid on the ordinary stage A; the crystal-plate C is then laid in position and the mark refocussed by raising the microscope and its objective D by the necessary amount FF′, that is *d*, and a second reading is taken for this position; lastly the upper surface of the crystal-plate is focussed and a third reading taken. The difference between the first and third readings gives *t*, the real thickness of the crystal-plate, while that of the second and third gives *t′*, the apparent thickness of the plate, as will be evident from the drawing (*b*) of Fig. 845. Then the desired refractive index of the crystal μ is at once obtained by dividing *t* by *t′*. The amount of raising, the value of $d = t - t'$, increases not only with the thickness of the plate but with the refractive index.

When the crystal is a doubly refractive one, it will obviously only be the mean refractive index which will be afforded by this determination. Sorby[1] in the year 1877 endeavoured to render it possible to determine the two different refractive indices of the two transmitted rays by use of a glass micrometer or crossed grating, consisting of fine lines ruled $\frac{1}{100}$th of an inch apart in two directions at right angles to each other. For the two sets of lines focus at different positions, the theory for which was worked out by Stokes. An excellent account of Sorby's work, brought up to the year 1909, appeared in the *Mineralogical Magazine* for that year,[2] the manuscript of which was prepared for the press by Sorby himself during his last illness. The lattice-plate was placed some little distance underneath the stage, with an iris diaphragm just above it and an achromatic condenser provided with a small stop immediately above, which focussed the lines at about the level of the stage. Below the grating a rotatable Nicol prism polariser could be thrown in or out of position, and an analysing Nicol similarly over the eyepiece. A cap pierced by a small hole was fitted over the objective in order to reduce the residual spherical aberration by stopping down to an aperture of 13°, and also a second cap was arranged to act as a semicircular stop, in order to cut off half the area of the objective field in any desired direction, the aperture of the front lens being circular. A scale and vernier attached to the stand and body-tube of the microscope completed the essentials. The reduced image of the lattice and of the aperture of the iris diaphragm, the latter adjusted to the most suitable small opening, could thus be readily focussed by the condenser on the under or upper surface of the plate of the doubly refracting crystal, or anywhere in its interior. According to the orientation of the section-plate with respect to the original crystal the appearances of such a grating are characteristically different.

For instance, when a plate of calcite cut perpendicularly to the axis is laid on the microscope stage and the grating examined through it, there are two positions, one exactly above the other, at which the image of both sets of lines of the lattice-grating is focussed by the microscope, rotation of the plate in its own plane making no difference.

[1] *Mineralog. Mag.*, 1877, *1*, 97. [2] *Ibid.*, 1909, *15*, 189

A cleavage plate of calcite, however, affords two images separated along the direction of the principal section of the plate, the one corresponding to the ordinary ray being in the centre of the field, and affording the ordinary index $\omega = 1{\cdot}658$. On rotating the plate in its own plane, this latter image remains central and undistorted, while the other corresponding to the extraordinary ray moves with the principal section and is elongated and coloured at the edges. When the principal section is parallel to either set of grating lines that set is alone visible, and the microscope tube has to be raised or lowered to focus the two images in such rectangular positions. The extraordinary image is thus bifocal, and is thereby distinguished from the ordinary image, which is unifocal, both sets of lines being simultaneously visible in the light of the ordinary ray at one and the same focus. The Nicol analyser can conveniently be used to discriminate between the ordinary and extraordinary images. The extraordinary image, of which the lines are parallel to the axis, is well defined and indicates an index of refraction of the value 1·412, while the image composed of lines perpendicular to the axis is blurred, the lines appearing as coloured bands in white light, but in red light they are sharp and afford the refractive index 1·578. The true extraordinary index is intermediate between the two, namely, 1·486. Hence the extraordinary image is truly bifocal.

A plate of calcite parallel to the axis shows three images lying over each other, which are best separated by use of the Nicol prism analyser over the eyepiece. When the vibration direction of the Nicol is perpendicular to the axis of the crystal the ordinary image only is seen, and both sets of lines are equally focussed at once, and afford the ordinary index $\omega = 1{\cdot}658$. When the Nicol is arranged with its vibration direction parallel to the axis only the extraordinary images are seen, one set of lines at one focus and the other at another, the image of the diaphragm being elongated in perpendicular directions for the two positions. When the lines are seen parallel to the axis the true extraordinary index $\epsilon = 1{\cdot}486$ is afforded. The index for the perpendicular direction is no less than 1·868, which agrees with the calculations of Stokes. The order of the three foci below one another, on lowering the microscope tube, is as follows: (1) the extraordinary image elongated perpendicularly to the axis and with only the lines perpendicular to the axis visible, (2) the ordinary image, (3) the extraordinary image elongated parallel to the axis and with only the lines also parallel to the axis showing.

The section-plates of calcite employed by Sorby in these interesting experiments varied from 0·3 to 0·4 inch in thickness. The objective found most convenient was a $\frac{2}{3}$-inch, with a No. 2 eyepiece. The use of the semicircular stop over the objective front lens has the effect of causing the ordinary ray to be well polarised in a plane perpendicular to the edge of the semicircular stop, and the extraordinary ray in the opposite sense, thus facilitating their identification.

It is remarkable that although quartz has such a weak double refraction it can be clearly recognised by Sorby's method. In a

section $\frac{1}{5}$th of an inch thick, cut perpendicularly to the axis, it is just possible to distinguish two foci, and in one cut parallel to the axis to see that there is both a unifocal and a bifocal image.

In the case of a plate of a biaxial crystal—rhombic aragonite and barytes being good examples investigated by Sorby, section-plates about $\frac{2}{5}$ths of an inch thick having been used—cut perpendicularly to one of the principal axes of the optical ellipsoid, two bifocal images are always observed, comparable to the two extraordinary images seen in the case of calcite or other strongly doubly refractive uniaxial crystal. In the case of calcite cut perpendicularly to the axis neither the ordinary nor the extraordinary image is polarised, unless the semi-circular stop be used in front of the objective; but in the case of a biaxial crystal cut perpendicularly to an axis of the ellipsoid the phenomena resemble more closely those seen in a plate of calcite cut parallel to the axis, where the extraordinary ray is clearly bifocal, which it is not in the case of the section perpendicular to the axis. Also with a biaxial crystal both the rays have this bifocal extraordinary character. The phenomena with biaxial crystals are thus very complicated, there being usually four different apparent indices of refraction. From the total results with several plates cut perpendicularly to at least two axes of the ellipsoid Sorby was able, however, to calculate the three true indices, α, β, and γ, from these apparent indices, with very fair accuracy to the third place of decimals.

The following laws were eventually arrived at by Sorby as to the general relations between the images observed and double refraction:

1. Crystals having no double refraction have no bifocal image.
2. Crystals having one axis of double refraction have one bifocal image.
3. Crystals having two axes of double refraction have two bifocal images.
4. Other circumstances being the same, the distance between the foci varies directly as the intensity of the double refraction, and directly as the thickness of the specimen.

The only exceptions are in the cases of very strongly dichroic substances like tourmaline, in which one ray is absorbed; tourmaline transmits only the extraordinary bifocal image, the ordinary ray being invisible through very dichroic green specimens, although slightly visible in less dichroic specimens.

There is no difficulty in carrying out Sorby's method in the cases of unifocal images, such as either the single one of a cubic crystal, or the ordinary image of a non-dichroic uniaxial crystal. For the apparent index of refraction is here also the true index, whatever be the orientation of the plate.

In the case of the single extraordinary bifocal image of a uniaxial crystal the true extraordinary index μ' can be conveniently determined, when the section is either parallel or perpendicular to the axis, from the equation $\mu' = \sqrt{\mathrm{A}\mu}$, in which A is the apparent index, the ordinary index μ being first determined and the two images being distinguished

by use of the semicircular stop over the objective. When the section is parallel to the axis, the apparent index a for lines parallel to the axis and perpendicular to the plane of polarisation is actually the true index μ' of the extraordinary ray; it may also be calculated from the other apparent index b by means of the equation $\mu' = \frac{\mu^2}{b}$. The value of μ' is thus obtained in duplicate from two different measurements, and when the results are concordant the mean may be accepted as the truth.

When the crystal has two bifocal images, polarised in opposite planes, as in the cases of biaxial crystals, giving the four apparent indices a, b, c, d, the three true indices of refraction μ, μ', μ'' may be either directly observed or calculated, when the section lies in the plane of any two of the three axes of the crystal. The apparent indices a, b, c, d then become respectively $\frac{\mu''^2}{\mu'}$, μ', μ, $\frac{\mu''^2}{\mu}$. The apparent indices b and c for lines perpendicular to the plane of polarisation are thus the true indices μ' and μ, while μ'' may be determined from the values of a and d by means of the equations $\mu'' = \sqrt{a\mu'}$ and $\mu'' = \sqrt{d\mu}$.

In the cases of determinations with crystals covered with thin glass cemented by Canada balsam, allowance is made for the combined layer of glass and balsam by deducting 0·53 of its value from both t and d; for the index of refraction of the combined layer is 1·53, and the focal length is therefore increased 0·53 for every 1·00 in the apparent thickness of the glass as measured by looking through it, the upper surface being focussed with the aid of dust particles, and the lower one by means of the markings or scratches on the surface of the crystal. The value of t must, of course, be reckoned from the apparent upper surface of the crystal and not from the top of the cover-glass.

Monochromatic light is essential to accuracy with the method; Sorby used a red glass, which gave results for the middle of the red end of the spectrum.

Section-plates need not be cut if there are natural crystals available with two opposite sufficiently flat faces; and it is only necessary that in some one part the crystal should be adequately transparent over a surface which need not exceed $\frac{1}{20}$th of an inch square. Perfect freedom from impurities is by no means essential, many good observations being possible with specimens loaded with fluid cavities and minute crystal or granular enclosures. But it is of prime importance that the crystal should not have a laminar or fibrous structure, giving rise to optically discontinuous planes, as they produce distorted images by internal reflection. Irregularities of surface may be almost completely overcome by enclosing the crystal in a liquid of approximately the same refractive index between the thick supporting glass and the cover-glass. But it is usually advantageous to polish the faces, if results of high accuracy are desired. The crystal or section-plate employed should have a thickness somewhere between the limits of $\frac{1}{10}$th and $\frac{1}{2}$ inch, and if the orientation of the section be not known, it can often be ascertained by the direction of elongation of the extraordinary images of the iris diaphragm, reduced

to a small opening in order to act as a spot of light. Indeed, Sorby recommends studying the images of this spot before passing on to observe those of the grating, and gives in his 1907 memoir a series of photographic reproductions of their appearance with various crystals.

The practical use of Sorby's method, however, is not very great; for crystals suitable for use by it are usually procurable sufficiently large for the measurement of the refractive indices by the method of the 60°-prism or that of total reflection. It is highly instructive and interesting, however, and may at any moment prove useful as a last resort. For further details of the interesting phenomena observed by Sorby with numerous minerals, the posthumously published 1907 memoir (*loc. cit.*) should be consulted.

(*b*) **The Immersion Method.**—The refractive indices of small crystal-plates and crystal-grains can be determined approximately under the microscope by observing the effects produced when they are immersed in a liquid of as nearly as possible the same refractive index. The method appears to have been first used by O. Maschke in the year 1871, and further elaborated by Schröder van der Kolk in 1892. If the index of the crystal be the greater, the crystal acts as a lens in increasing the convergence of the beam of incident light rays; and conversely, if the refractive index be lower than that of the liquid, greater divergence of the incident light is caused. If the objective be raised slightly from the position in which the crystal is focussed, the intensity of the light will appear to increase towards the centre of the crystal-plate or grain if the latter be more highly refracting than the liquid, a bright fringe appearing to wander towards the centre of the crystal. Conversely, when the liquid is more highly refractive the bright fringe wanders away from the centre until it forms a halo around the crystal when the objective is raised. A wide cone of light is to be deprecated, one of 5°-10° being ample, filling only one-half of the back lens of the objective. The aperture of the condenser should, therefore, be diminished by lowering it or by closing more completely the sub-stage iris diaphragm so as to form a very small stop, or best of all by doing both. A narrow beam of only feebly convergent and almost parallel light is then obtained, and differences of refractive index in different parts of the field are then more clearly visible. Frequently the light from a window subtending 5°-10° is found a very good source.

The effect is much enhanced by causing the incident light to be obliquely incident. This is best achieved, in spite of many special devices of stops and diaphragms, by simply shading a portion of the field by placing the finger in front of the reflector or polariser. Only the lower power objectives are required or desirable, so that the relative refraction of the whole aggregate of crystal-sections in the field of an ordinary thin section (mounted on a micro-slip as usual) can be observed at once. The most accurate work is done with monochromatic rather than white light, however, an intense sodium flame being admirable for the purpose. But valuable colour indications are also obtained by use of white light.

Supposing the finger to be used as above stated, to shade about one-half (one side) of the field, and that the crystal under observation is in

the bright part or mostly so, the following facts are observed: If the refractive index of the crystal be higher than that of the liquid, the edge of the crystal-section adjacent to or partially within the shaded half will appear brighter than the surrounding field and the opposite (farther) edge will be darker. Conversely, the farther edge is brighter and the edge near or in the shade is darker, when the liquid is the more highly refractive. When both crystal and liquid have exactly the same refractive index for sodium light or for a middle yellow ray about wave-length 0·000555 mm., and white light is used, the edge of the crystal nearest the shaded part of the field appears tinted orange-red, while the opposite edge appears pale blue coloured. It must be clearly understood, however, that the condenser has been lowered somewhat from its normal position, for this order of phenomena to be observed. If, however, the condenser be raised somewhat instead, the above appearances are reversed. Indeed, it is best to observe under both conditions, as one is then quite certain of the nature of the phenomena under observation, and that the position of the condenser is that which it was desired to be; the second series of obverse phenomena also afford an excellent confirmation of the conclusions as to the relative refractive indices of the crystal and the liquid. The rule should be thoroughly tested with substances of known refractive indices before any original work is proceeded to.

Another mode of stating the rule is as follows: When the obliquely incident light approaches from the left, a bright band of light appears on the right-hand margin of the crystal if it be more highly refractive than the liquid or other medium forming the rest of field, but on the left-hand margin if the crystal be of lower refraction than the field. When the light approaches from the right, the bright band appears on the left margin of the more highly refractive crystal, but on the right-hand margin if the crystal be less refractive. Or generally, in the case of excess refraction on the part of the crystal, the concentration of light in a bright band appears on the opposite side of the crystal to that on which the light is incident, and on the same side if the crystal be less refractive than the liquid or other medium of the field.

Liquids are generally more dispersive than crystals, and so if equality of refraction be attained for the middle of the spectrum, say yellow or green (about wave-length 0·000555 mm. is a good position to aim at), this equality is usually no longer true for the ends of the spectrum. For the red end the crystal will be more refractive, and for the blue end less refractive. Hence, the red rays are concentrated along one edge of the crystal-plate or grain, and the blue rays along the opposite margin, the crystal thus appearing fringed on its two opposite sides, near to the oncoming rays and away from them, with red or blue colour. If equality has been attained for about wave-length 0·000555 mm. the intensity of the two colours is equal. The red rays will be on the right edge and the blue rays on the left side of the crystal.

As an additional proof that identity of refraction for the middle of the spectrum has been attained, it will be observed, when the screening finger is removed from between the reflector and the polariser and ordinary

illumination is permitted to occur, that when the objective is raised the red rays wander towards the centre of the crystal, while the blue rays recede away outside the margin all round, so that the crystal appears orange-red set in a blue background. On lowering the objective the reverse occurs, the crystal appearing pale blue and ringed round with reddish-orange colour.

When monochromatic light is used, the refractive index can be determined by this immersion method to ± 0·001, and with white light to ± 0·005.

If the crystal belong to one of the doubly refractive systems, as will most frequently be the case, the two refractive indices (if it be uniaxial) ω and ϵ, or the three refractive indices (if it be biaxial) α, β, γ, can be determined in turn by placing the polarising Nicol in position, and adjusting the crystal in successive positions such that each principal axis of the optical ellipsoid in turn is parallel to the plane of vibration of the light from the polariser. Usually the two refractive indices α' and γ' will be afforded by a casually orientated biaxial plate, corresponding to vibrations parallel to the two principal axes of the section of the ellipsoid by the plate, in accordance with Biot's law (pages 897 and 1209). The principal refractive indices will only be obtained when the system or crystal-grain is normal to a bisectrix of the optic axial angle or an optic axis, or in general perpendicular to one of the three principal axes of the optical ellipsoid.

The following set of liquids has been recommended by F. E. Wright for use in preparing a series of media differing from each other in regular stages by 0·005 of refractive index:

Refractive Index for Na-light.	Liquid Mixture.
1·450 – 1·475	Petroleum and turpentine.
1·480 – 1·535	Turpentine and ethylene bromide or oil of cloves.
1·540 – 1·635	Oil of cloves and α – monobromonaphthalene.
1·640 – 1·655	α – Monobromonaphthalene and α – monochloronaphthalene.
1·660 – 1·740	α – Monobromonaphthalene and methylene iodide.
1·740 – 1·785	Sulphur dissolved in methylene iodide.
1·790 – 2·050	Methylene iodide, arsenic sulphide, sulphur, and tin iodide.

Each liquid is kept in a small dropping-bottle with ground-glass stopper and cap. Their refractive indices decrease by about 0·001 for every 3° C. of rise of temperature.

The oblique illumination method at once throws all the elements of the microscopic field into relief, and the contrast between the higher and lower refracting crystals is sharply brought out. For instance, lower refracting grains of orthoclase felspar in a thin rock section surrounded by the more highly refracting plagioclase felspar appear as small pits in the slide. Either a thin section, or powder (crystal-grains), mounted on a micro-slide in the liquid chosen, may be used.

Determinations with an orientated section, normal or parallel to the

optic axis (if uniaxial) or perpendicular to an axis of the ellipsoid (if biaxial), are always preferable, of course, if such sections can be found.

(*c*) **The Becke Line Method.**—This is a method applicable to closely adjacent crystals in a thin section, or even in sections somewhat thicker, which enables their relative refractive indices to be determined. In conjunction with the immersion method it enables the absolute refractive indices to be determined, to about the same degree of accuracy as has been specified for oblique illumination by that method, namely, when sodium light is employed to ± 0·001, and with grains even so small as 0·01 millimetre diameter.

The field is illuminated by a narrow cone of light from the condenser, and is clearly focussed and regarded through a very small stop restricting the eye-hole of the eyepiece. The light is then seen to be concentrated along the margin of the more highly refractive of the two adjacent crystals under observation, and on raising or lowering the objective from the focussed position forms a definite bright band, fringe, or line, known as the " Becke line " owing to its first description by F. Becke. This intense band of white light, the Becke line, is observed during the movement of the objective to move more and more towards or away from the junction between the two crystals, parallel to the line of junction. The rule is that on raising the objective the Becke line moves towards (farther inside) the crystal of the higher refractive index. High-power objectives are best employed in this method of the Becke line, because of their higher numerical aperture and consequent sharper resolution in depth. If the aperture of the sub-stage condenser be not sufficiently decreased, the light is concentrated on both sides of the boundary plane, and two Becke lines are seen, moving in opposite directions, which is very confusing. The remedy is to reduce the aperture of the cone of illumination, just as for the oblique illumination method, by lowering the condenser and closing more completely the iris diaphragm. The same remarks as to the preferable use of crystal sections normal to a bisectrix or to an optic axis, when obtainable, apply as for the oblique illumination immersion method ; the true refractive indices ω or ϵ, or α, β, and γ, can then be determined directly. Otherwise only the refractive indices corresponding to vibrations parallel to the principal axes of the elliptic section of the optical ellipsoid by the crystal-section plane are afforded (law of Biot; see page 897). J. W. Evans recommends that the section be examined under parallel Nicols with the planes of vibration of the adjacent crystal-plates equidistant from the principal Nicol planes. Owing to the high-power objective used, only two adjacent crystals can as a rule be examined in one field.

The Becke white-line effect is less distinct when the two crystals are embedded in a medium of markedly lower or higher refractive index, so that it is better to mount the section in a medium of about the same refractive index, and best of all of intermediate refractive index between the indices of the two adjoining crystals under comparison.

The explanation of the Becke line at first given was not satisfactory, as it dealt only with crystals joined by a junction at right angles to the

plate, a condition only rarely present. It also assumed the use of convergent light, although it has been admitted that too large a cone will destroy the effect, and practically the only case ever found to answer well in practice is when the nearest approach to parallel light is attained of which the microscope is capable.

A more satisfactory explanation has been given by G. W. Grabham,[1] who has studied the various possible cases of oblique junctions. These are reviewed at A, B, C, and D in Fig. 846.

The crystal of higher refractive index is always supposed to be on the right, as shown. The first diagram at A shows the incident rays bent on entering the denser medium, in the direction of the latter. The second at B shows them totally reflected back again into the denser crystal, and the third at C shows them entering the lighter from the denser medium and again being refracted towards the denser crystal. Indeed, whatever be the inclination of the junction the light traversing it is always bent towards the denser more highly refracting crystal. The fourth diagram at D explains why the white line is seen parallel to the junction when the microscope tube is slightly raised or lowered. Ray 6 meets the junction

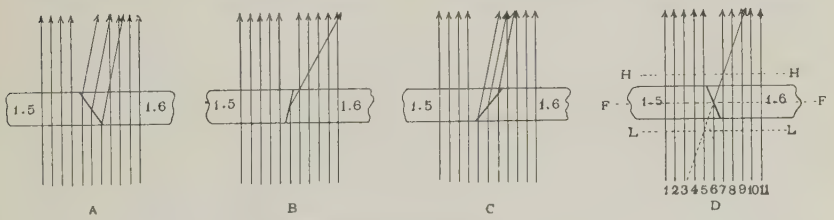


FIG. 846.—Explanation of the Becke Line.

and is bent towards the more highly refractive crystal on the right. When the focal plane of the objective lies centrally, about the position F, the section is in focus and no white line is seen at the junction. But when the tube is raised, say to bring the focal plane higher to H, a white line is seen on the side of the more highly refractive crystal, owing to rays 6 and 7 being brought to a focus as if they originated at their point of intersection on the focal plane. When the tube is further raised the point at which ray 6 meets the focal plane will coincide successively with rays 8 and 9, so that the white line becomes removed farther and farther to the right away from the junction (farther within the more highly refractive crystal). On the other hand, if the microscope be lowered, say to bring the focal plane lower to L, for a similar reason the white line moves to the left. In the case when the junction is truly normal, a certain amount of the light would still meet it obliquely and produce the line of white light as shown by Becke. But the other cases just dealt with are very much commoner.

An instance may be quoted from Grabham's memoir as an example. It was a plate of quartz, one half of which was cut normally to the optic axis and the other half parallel to the axis. When the polariser was

[1] *Min. Mag*, 1910, *15*, 341.

set so that the plane of vibration was parallel to the optic axis the greatest difference between the retardations in the two sections was produced, $\epsilon - \omega = 1{\cdot}5534 - 1{\cdot}5443 = 0{\cdot}0091$, as the beams transmitted by the two sections corresponded to the ordinary and extraordinary rays respectively. Although small, this difference in retardation is sufficient to produce a pronounced white line, and less than half a degree of deviation was found adequate. The deviation due to differently inclined junction planes amounts to as much as 12°, sufficient to throw the beam out of the field. The best white line is shown for a well-marked intermediate amount of deviation.

If oblique illumination be used when employing the method of the Becke line, the rays of light passing through the junction of two crystals are deviated towards the more highly refractive crystal, so that this latter crystal stands out with a light margin towards the finger or stop shadow, and a dark one on the side away from the shadow.

Use of an Adjustable Slit.—In the case of a thin crystal-section cut at right angles to a plane of symmetry of the optical ellipsoid, or of a crystal-grain arranged with a plane of optical symmetry at right angles to the microscope stage, it has been recommended by J. W. Evans [1] that a diaphragm with an adjustable slit, similar to that of the spectroscopic accessory (Fig. 841, page 1167), should be employed in order to isolate the direction of vibration perpendicular to the principal plane of the optical ellipsoid in question. The slit is to be arranged parallel to this plane, so that all the paths of the light rays passing it and illuminating the portion of the crystal in the axis of the microscope lie in the plane. On inserting a Nicol, with its vibration direction at right angles to the plane in question, the image of the crystal seen will be illuminated with light vibrating only perpendicularly to the plane, thus affording a definite, single, principal refractive index.

If the section be at right angles to two planes of optical symmetry (two such planes being thus parallel to the microscope axis), each may in turn be arranged parallel to the slit, and thus two of the three indices of refraction α, β, γ may be determined directly. In the simpler case of a uniaxial section the ordinary vibrations corresponding to the refractive index ω are determinable directly with any section, and a section parallel to the optic axis will give both the ordinary and extraordinary axial vibrations, and thus ω and ϵ, directly.

By such use of the slit accessory the method of de Chaulnes may be employed without being troubled by the Sorby bifocal effects, which are eliminated. The slit may also be used with advantage with the oblique illumination method of Maschke and Schröder van der Kolk; but the finger or other screen must be introduced along the direction of the slit-length. The slit is also applicable to the Becke line method, provided the slit be arranged parallel to the junction of the two crystals under observation and comparison. It gives as good results as a circular aperture of diameter equal to the slit width, while affording by its relatively great length very much better illumination.

[1] *Min. Mag.*, 1917, *18*, 130.

The slit may either be inserted under the stage instead of and in the place occupied by the iris diaphragm, or even closer to the object; or it may be placed in a slot at the focus of the eyepiece, where the directions-image (that afforded by convergent light) is usually formed by the Bertrand lens. In this latter case, the object-image formed above the eyepiece may be observed with a suitable lens, such as the Becke lens to be described in the next section.

Isolation of the Directions-image of a Small Crystal by the Becke Lens. —By directions-image is to be understood an image in which every point represents a direction followed by one of the light rays before reaching the objective; the interference figure afforded by a section-plate perpendicular to an optic axis or principal axis of the optical ellipsoid (bisectrix of optic axial angle) in convergent polarised light is an example. It has clearly to be distinguished from an ordinary object-image, the image of an object on the stage, focussed by the microscope in the ordinary way. It is often required to isolate a directions-image from a relatively very small object, such as a single minute crystal in a thin section, by some sort of diaphragm to cut off all light not from the object in question. The diaphragm must either be close to the object, or in a focus conjugate to it, so that the image of the diaphragm aperture and that of the object are seen together.

An excellent method of accomplishing this has been described by F. Becke. Instead of inserting the Bertrand lens in the tube, the directions-image is obtained by placing over the ordinary eyepiece a lens or system of lenses essentially similar to a Ramsden eyepiece, in an accessory fitting known as the Becke lens. It is shown in Fig. 847 as constructed by Swift. It magnifies the small directions-image which is formed in the Ramsden circle. The object-image is first observed in the focus of the eyepiece in the usual manner, and the object itself brought to the centre of the field. A diaphragm is then inserted through a slot in the focus of the eyepiece, so that only the object under investigation is visible. The Becke lens is then placed in position, and the directions-image will be seen quite free from undesired light. The advantage of this method of isolation is that the real object-image is considerably magnified, thus facilitating adjustment. Also a micrometer scale for measurement of the directions-image can be inserted at the focus of the lens. In the form shown in Fig. 847 the micrometer is adjustable, and can be used with the greatest facility for the measurement of the separation of the optic axial hyperbolic vertices.

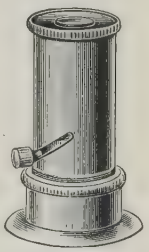


FIG. 847.
The Becke Lens.

A Becke lens of this description may also be used in the same manner, for isolation purposes, instead of the Bertrand lens, in the universal goniometer of Hutchinson described on page 1035, when converting the optical tube of the latter from a microscope into a telescope focussed on infinity.

For determining the angular position of a point in the directions-image J. W. Evans[1] uses a circular disc of white metal, similar in size to the

[1] *Min. Mag.*, 1916, *18*, 54.

circular stage of the microscope, and raised slightly above the latter so as to clear the slide; on its polished surface a network of concentric and radial lines is engraved, a circular hole being left in the centre of the plate so that the crystal can be observed through it. The radial lines are engraved at 5° intervals, and the concentric lines at distances from the centre equal to $r \tan \theta$, where r is a convenient length, such as 50 mm., and θ represents successive angles differing by 5°. The net is, therefore, a gnomonic projection of the points where a sphere is intersected by lines at equal intervals of azimuth and of angular distance from the normal to the plate at the centre.

Direct Measurement by Babinet's Compensator of Retardation and of Strength of Double Refraction in a Crystal Plate. It is often required to determine the difference of the two refractive indices μ_1 and μ_2, that is, $\mu_2 - \mu_1$ where $\mu_1 < \mu_2$, for any particular section-plate that may happen to be available. In the cases of plates orientated parallel to the optic axis, or perpendicular to the β axis of the optical ellipsoid, such a determination is of further importance as affording the amount of the double refraction for the whole crystal, the difference between the two, or two extremes of the three, refractive indices of the substance. The most satisfactory mode of carrying out the determination is by means of the compensator of Babinet, described in the last chapter, and illustrated in Figs. 836 and 837, page 1163.

The interference colour exhibited by a crystal-plate of thickness l is the same as that of an air film the double thickness $2h$ of which is equal to the product of l and the difference of the two refractive indices, μ_1 and μ_2, corresponding to the two rays propagated in the direction normal to the plate. That is:

$$2h = l\,(\mu_2 - \mu_1).$$

When the plate is one of a uniaxial crystal parallel to the axis, the two rays propagated along the normal to the plate vibrate respectively parallel to and perpendicular to the axis, and correspond to ϵ and ω, so that $\mu_2 - \mu_1$ becomes the important constant $\epsilon - \omega$ or $\omega - \epsilon$, the maximum amount of double refraction for the whole crystal, according as the latter is positive or negative. Also, when the plate is one of a biaxial crystal cut parallel to the plane of the optic axes, one of the rays transmitted along the normal (the direction of the intermediate axis of the indicatrix β) will vibrate parallel to the α axis of the optical indicatrix and the other parallel to the γ axis, the former direction α being that of the acute bisectrix of the optic axial angle (first median line) when the crystal is negative, and that of the obtuse bisectrix (second median line) when the crystal is positive. Hence the two vibration directions of such a plate correspond to the maximum and minimum refractive indices of the whole crystal, and thus such a plate affords $\gamma - \alpha$ (μ_2 here $= \gamma$ and $\mu_1 = \alpha$), the maximum amount of double refraction of the crystalline substance.

The actual determination of the difference of the two refractive indices, and of the actual amount of retardation R of one of the rays transmitted by the crystal-plate behind the other, is carried out with the

aid of Babinet's compensator as follows: The compensator is arranged with its quartz wedges at 45° to the crossed Nicols, and with the movable wedge arranged at its zero position, that is, so that when white light is used the black central band is arranged altogether and symmetrically between the pair of parallel spider-lines. The doubly refracting crystal-plate under investigation is then introduced on the microscope stage, so that its extinction directions (the traces of its vibration planes) are also at 45° to the crossed Nicols. It will then be observed that the bands have been displaced, so that the black band is no longer between the two spider-lines, but may be several bands away. Monochromatic light of wave-length λ, say sodium light, wave-length 0·000589 mm., is next employed, and the amount of displacement d, the movement of the movable wedge required to bring the black band back to its original zero position between the two spider-lines, is measured in scale divisions and (for the fractional part of a division) drum readings. The difference of path of the two rays or retardation R of one ray behind the other, brought about by the passage through the crystal-plate, is then given in millimetres by the expression $R = Cd$, in which the only unknown quantity is C, the constant of the compensator, the value of the scale divisions in bands of known retardation.

The retardation R at any point is the difference of the two opposing retardations, r_1 and r_2, and these depend on the thicknesses t_1 and t_2 of the two wedges at the point, and on the known difference of the refractive indices of quartz ϵ and ω. In fact, $R = r_1 - r_2 = (\epsilon - \omega)\ (t_2 - t_1)$, for it is the same as is given by a plate of thickness $T = t_2 - t_1$. It will be clear from Fig. 848 that by the sliding of the wedge the total thickness is increased by ΔT, entirely due to extra material of the movable wedge, that is, $t_2 - t_1 = \Delta T$, as the amounts were equal at the zero position; also that the displacement $d = \Delta T/\tan\ \alpha$, where α is the angle of the wedge. This ΔT is the compensation thickness required to neutralise the effect of the crystal-plate of thickness t and indices μ_1 and μ_2. Hence,

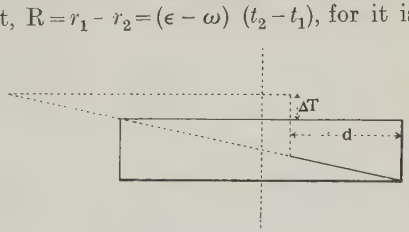


FIG. 848.

$$\Delta T\ (\epsilon - \omega) = t\ (\mu_2 - \mu_1).$$

The Determination of the Constant of the Compensator, C, is readily carried out by first taking the reading in white light for the adjustment of the black band to the centre of the pair of parallel spider-lines, the separation of which is adjusted to be only just slightly greater than the width of a band, and then illuminating with sodium or any other convenient monochromatic light of known wave-length; each other band, on both sides of the centre, is then brought in turn into the central position between the two spider-lines, and the reading taken for each such adjustment of a band. What we really do is to determine the amount of displacement d required, for the particular light used, to bring

about a difference of path equal to one wave-length of that light, for instance 0·000589 mm. when Na-light is employed. For it will be remembered that the centre of the first band on either side of the central one corresponds to one wave-length difference, λ, from the centre of that central band, as explained on page 1165 of Chapter LII., and that each successive band is due to a further retardation of a wave-length. We have, therefore, the data given in the second column of the following table for crossed Nicols. A similar set of readings, corresponding to the data given in the third column of the table, can also be taken for the bands produced in the intermediate position when the Nicols are parallel.

Table of Retardations for Sodium Light.

No. of Band from Centre.	Retardation R corresponding to Production of Band.	
	Nicols crossed.	Nicols parallel.
1	$\lambda = 0{\cdot}0005893$ mm.	$\lambda/2 = 0{\cdot}0002946$ mm.
2	$2\lambda = 0{\cdot}0011786$	$3\lambda/2 = 0{\cdot}0008839$
3	$3\lambda = 0{\cdot}0017679$	$5\lambda/2 = 0{\cdot}0014732$
4	$4\lambda = 0{\cdot}0023572$	$7\lambda/2 = 0{\cdot}0020625$
5	$5\lambda = 0{\cdot}0029465$	$9\lambda/2 = 0{\cdot}0026518$

The constant C is thus $C = R/d$, where R is the actual retardation in millimetres for any band, and d the displacement of the band from the central position in drum units. C may thus be determined ten times over, for the five bands on each side of the central black one. The interval in scale and drum readings between every two consecutive bands for the same wave-length should be the same, but when it is not, a curve should be constructed expressing the values. The value C of a drum unit in actual retardation is thus obtained. If it be desired to make determinations with other wave-lengths, the constant C can either be determined directly for these wave-lengths, or calculated from the knowledge of the dispersion of quartz.

If now, on introducing a doubly refractive crystal-plate, the displacement of the central band be equal to, say, 3·5 bands, the *Retardation* R will be :

$$R = Cd,$$

where d is the displacement corresponding in scale divisions and drum readings to the 3·5 bands, and C is the retardation value of a drum unit as above determined for the wave-length of the light employed.

Finally, the *Double Refraction*, the difference of the two refractive indices is :

$$\mu_2 - \mu_1 = R/t,$$

where t is the thickness of the crystal-plate.

For the more convenient determination of the relative retardation of minerals in thin sections, a fixed double quartz wedge has been devised by Dr. J. W. Evans[1] and

[1] *Min. Mag.*, 1905, *14*, 91.

is constructed by Messrs. R. & J. Beck. It consists of two quartz wedges of identical angle mounted side by side close together, one with its length parallel to the axis as usual, and the other with its breadth parallel to the axis. When placed obliquely between crossed or parallel Nicols they show the same bands continued across both, which are unaffected when a crystal-plate is also introduced at its extinction position. But when the plate is rotated 45° a black band indicating the position of compensation is shown by one wedge, and enhanced retardation colours are displayed by the other. The colour opposite the black band indicates double the retardation due to the crystal alone, thus affording a delicate determination of the latter.

Determination of Extinction Angles under the Microscope.—It will be unnecessary to repeat here the principles underlying the determination of the extinction directions in a crystal-plate, as they have been so thoroughly dealt with in Chapter XLII. as regards the theoretical considerations involved, and in Chapter XLV. concerning the practical determination of extinction angles by the stauroscope. It will be sufficient to remind the reader that the operations can be carried out in a simpler, somewhat more limited and, therefore, correspondingly less accurate method, with the aid of the microscope arranged for parallel light; that is, the microscope is used without either sub-stage condenser and convergent system or the Bertrand lens, the only essentials besides the objective and eyepiece being the polarising and analysing Nicols and, if desired, one of the stauroscopic sensitiveness enhancers, described and illustrated in the previous chapter, such as the Bertrand quadruple-quartz-plate eyepiece, page 1159, Fig. 831, or the Calderon double plate of calcite, same page, Fig. 832. The mode of carrying out a determination of extinction with the aid of the Bertrand eyepiece of the Dick microscope has been fully set forth at the conclusion of the description of the latter on page 1159. If it be desired to employ a Calderon double plate instead, it is preferably introduced also in a special form of eyepiece, as shown in Fig. 832, in which form it is constructed very efficiently by Fuess, and which may quite conveniently be adapted to the Dick microscope as well as to the Fuess microscope itself. The eyepiece is of the negative Huyghenian form, the diametral cementation line of the two halves of the Calderon plate being clearly focussed by the eye-lens. The analysing Nicol fits above the latter, and is supplied with a covering cap with very small eye aperture, as in the case of the Nicol analyser of the stauroscope. A diaphragm with a small aperture is also placed just over the double plate in order to restrict the field and the light to the rays passing nearest to the axis of the microscope, the fine line of cementation being then sharply defined. The latter is arranged to correspond to the zero of the circle of the Nicol, as indicated by a mark on the eyepiece tube, and when this Nicol is crossed to the polarising Nicol the two halves of the plate show equal intensity of half-shadow, that is, appear almost dark to an equal extent. The crystal under observation is then arranged to be bisected by this line of cementation, just as in the stauroscope, and the stage carrying it is rotated, in order to determine the extinction position, until the two halves of the double plate are again of equal slight intensity of illumination (half-shadow) by the monochromatic light employed, as

they were before the introduction of the plate. The cementation line can quite conveniently be used as a cross-wire for the purpose of adjusting an edge of the crystal outline to it, the edge representing the foreshortened face of reference, perpendicular to the plate, with respect to which the extinction is being determined. The difference between the reading of the rotating stage circle for this position and that for the adjustment of the crystal to afford two equally illuminated halves is the extinction angle required. It should be determined several times, approaching the adjustment from both directions, and if possible with the crystal inverted for a second series of readings. The mean should then afford a close approximation to the truth.

Determination of the Crystal System.— A preliminary idea of the system of symmetry to which a crystal belongs can frequently be obtained with the aid of the microscope, especially if a Fedorov universal stage be available. A cubic crystal is isotropic in all directions, and unless in a condition of strain does not polarise in colour or afford any double refraction phenomena at all.

Uniaxial crystals appear isotropic along the one direction of the principal axis, which is the optic axis of no double refraction as well as the axis of tetragonal, hexagonal, or trigonal symmetry. Although they are doubly refractive in all other directions they can usually be distinguished from biaxial crystals at once by the fact that **every section of a uniaxial crystal contains one of the infinite number of equal diameters ω of the circular section of the indicatrix, perpendicular to the principal (the optic) axis.** This seems impossible at first sight, but on reflection it will be seen that any section whatsoever of an ellipsoid of revolution may be moved in imagination parallel to itself, which obviously does not affect the optical phenomena which it displays, until it passes through the centre of the ellipsoid, if it does not already do so. The minimum or maximum axis of the elliptical section of the indicatrix, made by the plate, according as the crystal is positive or negative, will then in all cases be a diameter of the circular section of the optical indicatrix; in other words, it will always be one of the infinite number of directions in the circular section the vibrations along which correspond to the refractive index ω. Therefore, **one of the two directions of extinction in a uniaxial crystal-plate, cut anyhow, is always an equatorial diametral direction corresponding to the refractive index ω**, and the extinction direction at right angles to it will correspond to a direction in a principal section of the indicatrix ellipsoid of revolution, that is, to a direction in a section containing the optic axis, somewhere between ω and ϵ, the latter refractive index corresponding to the direction of the optic axis. A special case is when the section-plate happens to be parallel to the circular section itself, when every direction in it corresponds to ω and the plate remains dark on revolution under crossed Nicols, every direction being then one of extinction.

On examining one of the two rectangular directions of extinction in the general uniaxial case, and setting it parallel to one of the horizontal axes of rotation of the universal stage, it will be found that under

crossed Nicols such a general section will remain dark on rotation if the direction selected has been that of ω. But if the wrong one of the two has been chosen the section-plate will show the usual interference colours in parallel polarised light, unless the section-plate should happen to be one parallel to the optic axis, such as a plate or tabular crystal parallel to a pair of faces of the primary hexagonal or tetragonal prism zone, the discovery of which fact would of itself be of prime importance and simplify the work considerably.

When a tabular crystal perpendicular to the optic axis is available, discovered in parallel light by remaining dark on rotation in its own plane, and through which in convergent light under crossed Nicols the interference figure of circular rings and black rectangular cross is visible, the proof of the uniaxial character of the crystal will be complete. With the aid of the universal stage of Fedorov, or that of Klein, and even with the Miers stage goniometer, it is often possible to see the uniaxial interference figure through crystals not tabular when the crystal is immersed in the small cell containing a highly refractive liquid—the liquid chosen being one in which the crystal is most nearly invisible and therefore of like refractive index—and when the crystal is rotated until the optic axis is brought parallel to the axis of the microscope.

It is usually fairly easy to discriminate between a tetragonal and a hexagonal crystalline substance, for the former shows square or regular octagonal outlines sooner or later, when numerous crystals of the substance are examined, while the latter exhibits hexagonal 120° or 60° outlines, perpendicular to the optic axial direction. To discriminate between the hexagonal and trigonal systems is not so easy, unless obviously definite rhombohedra are characteristic. Further study of the nature of the end-faces, those other than the hexagonal prismatic forms which are common to the hexagonal and trigonal systems, is requisite, differences of surface of alternate faces of apparently hexagonal pyramids being particularly helpful. Angular measurements will probably require to be made before certainty is arrived at, and these may often be carried out with good microscopic crystals by the methods described earlier in this chapter.

A biaxial crystal, in general, does not remain dark when rotated about either extinction direction, and when it actually happens that the crystal under examination follows this rule its biaxial character is at once discovered. For if it were uniaxial it would remain dark when rotated about one of the two extinction directions. Only section-plates parallel to the primary zones, or natural plates, tabular crystals, parallel to the actual faces of these zones, do in the case of biaxial crystals remain dark on rotation about the extinction directions. The discovery of two directions of isotropism, the two optic axes, also affords immediate proof of biaxial character, and this discovery can often be made with the universal stage, especially when the crystal is immersed in a liquid of the same refractive index. For when such a direction is brought parallel to the axis of the microscope the crystal will remain dark when rotated under crossed Nicols in parallel light, and will show the rings and single brush of a biaxial crystal in convergent light. When rotated to the

intermediate direction, that of a median line, it will show the full biaxial interference figure, with the optic axes separated at either their acute or obtuse angle, unless the latter happens to be too large to be visible even in the highly refractive liquid; if this should be so, however, the perpendicular intermediate direction will afford the acute-angle figure. Indeed, the recognition of the biaxial interference figure in convergent polarised light is at once conclusive evidence of biaxial character, that is, of rhombic, monoclinic, or triclinic symmetry. It frequently happens that even a cursory examination of a number of crystals of a biaxial substance will reveal the figure, if not symmetrical to the centre, as it probably would be in the event of the crystal being rhombic, still not displaced from the centre too much for recognition of its nature.

When the crystal is rhombic the two rectangular extinction directions will as a rule either be parallel to two rectangular edges of the crystal as seen under the microscope, or symmetrical to two parallel pairs of edges. Also the biaxial interference figure will probably show itself, if not immediately, sooner or later on examining a number of crystals, symmetrical to the centre when a tabular crystal parallel to an axial plane is laid on the simple microscope stage. A monoclinic crystal will also in some cases show extinction directions parallel to rectangular faces, those of the ortho-zone, but such a crystal-plate will not be likely to afford an interference figure symmetrical to the centre of the field, although it may exhibit one symmetrical to a diameter, the trace of the symmetry plane. Other plates than those of faces in the ortho-zone will show extinctions oblique to the faces. Also, when the interference figure is closely regarded, discrimination between the rhombic and monoclinic systems can usually be effected by observing the nature of the dispersion shown by the figure in white light. When the crystal is rhombic the distribution of the colours will always be perfectly symmetrical, that is, both to the centre and to the two rectangular diameters parallel to the black cross formed when the plate is arranged parallel to the planes of vibration of the crossed Nicols. If monoclinic, it will show either horizontal, inclined, or crossed dispersion, as described at the conclusion of Chapter XLII. If the crystal be obviously biaxial, but exhibits none of the regular phenomena just referred to as typical of rhombic and monoclinic crystals, it can only be preliminarily considered as triclinic. It is much more likely to be really triclinic if it appears to be not very far from showing monoclinic phenomena, for instance, when the plane of the optic axes shows itself as only a very few degrees, yet clearly so, from being parallel to a crystallographic facial plane, than if the differences are greater. For we have always to reckon with the possibility that the crystal before us may belong to a class of the rhombic or monoclinic system of lower than full systematic symmetry. It could not be of higher symmetry, that is uniaxial, because even such low-symmetry classes of the uniaxial systems will always show the uniaxial interference figure sooner or later, whereas a biaxial crystal of lower than full systematic symmetry will yield a biaxial figure. Such difficult cases of apparently triclinic crystals absolutely necessitate angular interfacial measurements. Moreover, we

have always to remember that such crystals of low-class symmetry may belong to one of the eleven enantiomorphous classes, which may be expected to display optical activity. Hence, we have always to be on our guard that polarisation phenomena displayed are the regular ones due to double refraction, and not those due to optical rotation. The latter can always be recognised, and the angle of rotation measured in monochromatic light, quite conveniently under the microscope, provided the property be developed sufficiently strongly, which is rare, to exhibit it in plates or crystals as small as are generally investigated under the microscope. This disturbing cause is thus not so serious in microscopic work on account of the small size (thickness) of the crystals usually alone operated on.

Lastly, as regards the preliminary determination of the crystal system under the microscope, such observations should, unless no other observations are possible, only be regarded as truly preliminary, to be followed by definite angular measurements on a good goniometer, and by precise determinations of the optical constants on the accurate measuring instruments described in previous chapters. Such preliminary work with the microscope frequently very considerably facilitates the systematic investigation just referred to, as the observer knows his way about the crystals, and is familiar with their prominent characteristics. In cases where such further work is impossible, on account of inability to obtain or grow crystals of adequate size, this microscopic investigation is invaluable.

In the above statement it has been assumed that single individual crystals have been available. Simple twinning is immediately recognised under the microscope, as the two halves of a twin polarise differently. Even repeated twinning is likewise at once detected, provided it be not parallel to the plane of the stage, the various strips polarising so that adjacent individuals always show different colours on rotation of the stage or the Nicols, at some position or other during the rotation, four times repeated during a complete revolution, the Nicols being crossed. But, as has been pointed out in Chapter XXVIII. on twinning, microscopic laminated twinning often apparently enhances the symmetry, and may be so fine, the alternations so numerous, as to be ultra-microscopic with the low powers used. Moreover, the only crystals available may be entirely those composed of twin lamellæ parallel to the section-plate or tubular crystal faces, when very complicated optical phenomena are possible, as described in the section on Optical Anomalies on page 1144. Such cases require most careful and special investigation, including that with high-power objectives; indeed, it will be obvious that the microscope becomes here the ultimate instrument of research, and not merely one for preliminary examination. But it is largely because of such possibilities that an open mind should be maintained as long as possible as to the results of a microscopic investigation, and every effort be made to supplement them by regular large-scale measurements.

Discrimination of the Class of Symmetry by means of Etched Figures.—One of the most important uses of the microscope is the examination of etched figures on the faces of crystals, not merely on microscopic ones but even on crystals of some size, for the purpose of

definitely settling the particular one of the 32 classes of symmetry to which a substance conforms, the latter being known from the earlier part of an investigation to belong to a particular system.

Instead of invoking the ordinary rapid solvent action, of a solvent poured in quantity on the material of a crystal, the solvent is applied in these experiments in relatively very small quantity compared with the bulk of the crystal substance. For instance, to study the etched figures of a crystal soluble in water, the minute quantity of water may be applied by breathing on the crystal faces or slightly steaming them, or gently touching them once or twice with a damp cloth. The process of solution then begins at isolated spots instead of all over the surface, and occurs with different rapidity in different directions radiating from each of such spots, beginning first with the direction of least cohesion and, in fact, indicating the order of cohesion in the different directions, and therefore of the symmetry, by the character of the figure produced. Such etched figures are generally of the character of depressions or pits of specific shape, and their configuration is in accordance with the class-symmetry of the crystal, and forms perhaps the best of all indications of the detailed character of such symmetry. For the resistance to etching in different directions is obviously a direct outcome of the structure. The shape of all the pits on any particular face will be similar, and also on all faces of the same form, that is, on faces which are absolutely equivalent as regards the symmetry. Water, dilute acids, alcohol, ether, benzene, acetone, carbon bisulphide and other of the usual organic solvents, are the principal solvents employed, and the essence of effective treatment is to apply them in the minimum possible quantity, for instance, by merely touching with a cloth moistened with the solvent. Mineral crystals are often found with faces naturally etched by water containing carbon dioxide or other acid gases such as hydrogen chloride in solution, or by gaseous hydrogen fluoride or even by water at high pressure and temperature or by superheated steam. The etched figures obtained on crystals of right-handed and left-handed quartz by means of a very weak solution of hydrofluoric acid, for instance, are given in Figs. 314 and 313 on page 356.

It is important that adequate time should be allowed for the solvent to act to its full extent, otherwise immature etched figures may be produced leading to erroneous conclusions. A striking case is that of rock salt, sodium chloride NaCl, which was formerly wrongly considered to belong to the pentagonal icositetrahedral class 29 of the cubic system, on the evidence of immature etched figures of pentagonal icositetrahedra, whereas it is really holohedral, of class 32, longer action of the solvent producing hexakis octahedral figures.

Perhaps one of the most instructive cases that could be cited of the use of etched figures to discriminate between two classes and even two systems, is one to which particular attention has been called by Miers, namely, the effect of hydrochloric acid on apatite and calcite. Apatite has been shown in Chapters XX. and XXI. to belong to the bipyramidal class 25 of the hexagonal system, in which the elements of symmetry are

the essential hexagonal axis and the equatorial plane of symmetry, the six other symmetry planes and six digonal axes of the holohedral hexagonal class 27 being absent. The etched figures afforded by a hexagonal prism of apatite with hydrochloric acid are shown in Fig. 849, and the adjacent Fig. 850 illustrates the etched figures given under similar conditions by a hexagonal prism of calcite, which has been shown in Chapters XXII. and XXIII. to belong to the scalenohedral class 21 of the trigonal system. The essential trigonal axis of symmetry and three symmetry planes intersecting in it, together with three digonal axes lying in the equatorial plane midway between the symmetry planes, are the elements of symmetry present in calcite and its class. There is no equatorial plane of symmetry, as in the holohedral trigonal class 22, and the digonal axes differ from those of that class by not lying in the symmetry planes.

The first difference in the etched figures on the two crystals that strikes us is that in apatite they are the same on all the six faces of the

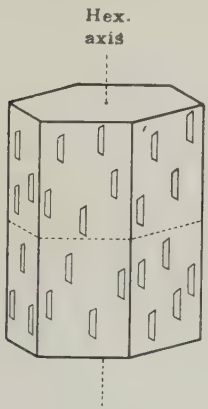


FIG. 849.—Etched Figures afforded by Apatite.

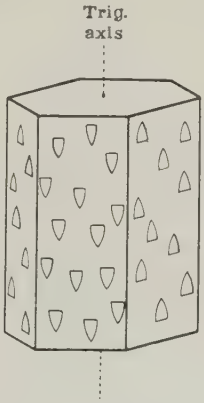


FIG. 850.—Etched Figures afforded by Calcite.

hexagonal prism, indicating truly hexagonal symmetry; while on calcite alternate faces bear differently directed figures, although the shape is the same, indicating that all the six faces belong to the same form, the pointed end, however, being upwards in one alternate set of three faces and downwards in the other, indicating trigonal and not hexagonal symmetry. It must be remembered that the hexagonal prism is a form common to both the hexagonal and trigonal systems. Moreover, each of the calcite etched figures is symmetrical to a vertical plane of symmetry, but not to an equatorial plane; and obviously the digonal axes do not emerge through the middle of the faces but through the edges, indicating class 21 and not the holohedral trigonal class 22. Again, the etched figures of apatite are symmetrical at both ends to the equatorial plane of symmetry, but not to vertical planes of symmetry, which are thus absent, indicating class 25 and not the holohedral hexagonal class 27.

As an instance of the etched figures of crystals of low but holohedral symmetry, an instructive series of etched figures on the principal faces of two members of the important monoclinic series of double sulphates of the series $R_2M(SO_4)_2 . 6H_2O$ may be referred to, and are reproduced in Figs. 851 and 852. They were obtained by H. Baumhauer[1] by means of a very small quantity of water, and their shapes conclusively prove the holohedral nature of the monoclinic symmetry. Fig. 851 shows the character of the etch-figures on the predominating faces of $r'\{201\}$ in the case of ammonium ferrous sulphate; for on the crystals of this salt the pair of faces of this form are exceptionally largely developed. Fig. 852 reproduces those on the four prin-

FIG. 851.—Etch-figures on Ammonium Ferrous Sulphate.

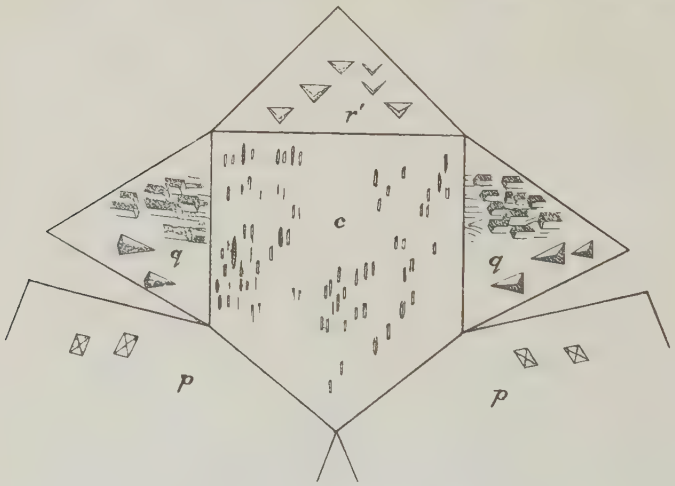


FIG. 852.—Etch-figures on Potassium Nickel Sulphate.

cipal forms $c\{001\}$, $p\{110\}$, $q\{011\}$, and $r'\{201\}$ of potassium nickel sulphate. Those on ammonium nickel sulphate were also obtained and found to be very similar. It will be clear that these etch-figures in every case are symmetrical to the single plane of symmetry $b\{010\}$, which is at right angles to the plane of the paper and parallel to the longer sides of the page; they also accord with the presence of a digonal axis of symmetry perpendicular to the plane of symmetry (parallel to the shorter edges of the page). They possess, consequently, both the elements of monoclinic symmetry, and therefore the crystals are holohedral.

[1] *Pogg. Ann. d. Phys.*, 1873, *150*, 619.

An excellent set of drawings of etched figures of all the 32 classes of crystals will be found on pages 280 and 281 of Miers' *Mineralogy*. Miers has further shown that the sides of etched figures are minute facets, vicinal faces of very high indices not perpendicular to any of the planes or axes of symmetry; he has made a profound study of the character of these vicinal faces, and an account of the highly interesting results has already been given in Chapter XXIV.

Determinations of Optic Axial Angles by the Microscope.—It will have been clear from Chapter XLII. that the interference figure in convergent polarised light is composed of curves or lines of two kinds. One of these consists of curves, circles, or lemniscates, commonly known as "rings," which are dark and luminous alternately when the polariscope is illuminated with monochromatic light. They become coloured when white light is substituted, and their form is independent of the position of the axes of the section-plate relatively to those of the crossed Nicols. They do not become deformed on rotation of the section-plate in its own plane, and their form has no connection with the direction of the original plane of polarisation. These curves of the first kind are exclusively due to interference, being "Isochromatic Curves of Equal Retardation." The curves of the second kind, commonly known as "brushes," remain dark when white light is used, the Nicols being crossed, but are colourless and bright when the Nicols are parallel. They alter in the case of biaxial crystals when the section-plate is rotated in its own plane, their form being connected, in the general case, with the extinction directions of the plate, and, in the special very important case of a plate perpendicular to the first median line, with the direction of the axes of the optical ellipsoid lying in the plane of the section-plate, relatively to the plane of polarisation of the rays received from the polarising Nicol. They are generically termed "Isogyres."

Curves of Equal Retardation.—Assuming the Nicols crossed, the interference is positive, causing a dark curve of equal retardation, when the retardation of one of the two interfering rays behind the other is equal to an odd number of half wave-lengths, that is, to $(2n+1)\lambda/2$. The interference is negative, producing a bright curve of equal retardation, when the delay is equal to an even number of half wave-lengths, that is, to $2n\lambda/2$ or $n\lambda$. We have to add to these retardations within the crystal, however, the half wave-length change of phase introduced by the action of the analyser, so that the total retardation observed due to both causes is really the reverse, namely, $2n\lambda/2$ or $n\lambda$ for a dark curve and $(2n+1)\lambda/2$ for a bright one, odd and even half wave-lengths corresponding to reversed phenomena compared with the usual effect of interference of light waves, as explained in Chapter XLII. pages 917, 919, and 921. When the Nicols are parallel the converse is true of the conditions for the two cases. These curves of equal retardation are given by the intersection of surfaces of equal retardation $\lambda/2$ (dark), $2\lambda/2$ (bright), $3\lambda/2$ (dark), $4\lambda/2$ (bright), and so on, by a plane parallel to the crystal section-plate.

Isogyres.—The intensity of the light transmitted by the analyser obviously depends not only on the retardation but on the orientation

of the planes of vibration in the crystal with respect to the Nicols; that is, on the directions of the axes of the elliptic section of the ellipsoid by the plate, the extinction directions, in the general case, and on the directions of the axes of the optical ellipsoid of which the crystal-plate is a principal section, in the special case of a section-plate perpendicular to the first median line prepared for the measurement of the optic axial angle. Such rays, therefore, as emerge vibrating parallel to the polariser, are stopped by the analyser when the latter is crossed to the polariser, and this extinction gives rise to the isogyres. They are clearly independent of the wave-length of the light employed. But their form is dependent in general on that of the optical ellipsoid, on the orientation of the section-plate with respect to the latter, and of the positions of the axes of the ellipsoid with reference to the vibration directions of the Nicols.

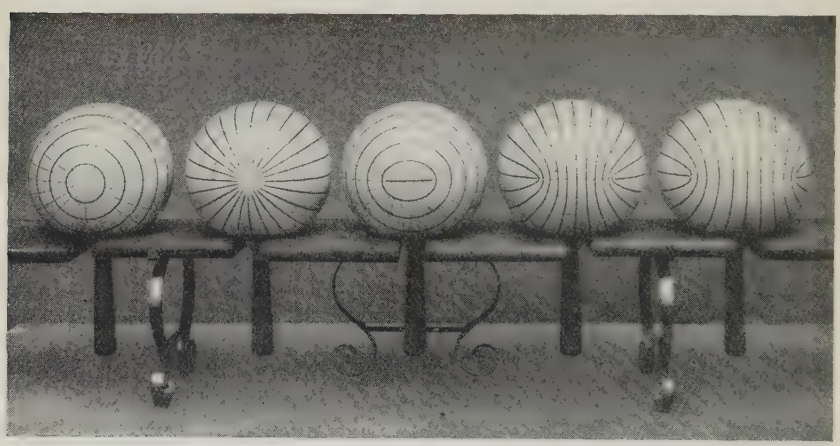


FIG. 853.—Spherical Models exhibiting Becke's Curves of Equal Velocity.

Curves of Equal Velocity and Skiodromes.—It has been necessary thus to summarise these facts here, as a résumé and somewhat of a further development of those given in Chapter XLII., inasmuch as some extremely interesting and important work in improving microscopic methods of attack has recently been carried out by F. Becke of Vienna and E. S. Fedorov of Petrograd, in which both curves of equal retardation and isogyres have their own important places. The form of the isogyres has been deduced by Becke[1] from the consideration of curves of equal velocity, to which he has applied the name velocity ellipses or "isotaques." A series of models are represented in Fig. 853, constructed by Krantz of Bonn, which represent these curves on a sphere, for a typical set of uniaxial and biaxial crystals, the actual models which the figure represents being in the Science Museum at South Kensington.

The two first are of uniaxial crystals, and the three others of biaxial

[1] *Min. und petrogr. Mittheil.*, 1905, *24*, 1 and 34.

crystals having optic axial angles respectively of 30°, 60°, and 90°. They give a general representation of the directions of vibration of the light waves in the crystal, for these directions at any selected point are the tangents to the two curves (drawn like lines of latitude and longitude on the sphere) which intersect at that point.

These curves of equal velocity, the isotaques, may also be projected in a stereographic projection, like the zones of crystal faces in our ordinary crystallographic stereographic projection. Their orthogonal projections have, however, been preferred by Becke, and used by him for the deduction of the shape of the isogyres, and such projections have been termed by him "skiodromes." While of great theoretical interest, however, skiodromes are not of much practical service, as the forms of the isogyres are so readily determined by actual observation, even if only by a microscopic method, and provided at least one of the biaxial pair be visible in the field of view. Such experimental determination is obviously far preferable, and the microscopic methods of Becke himself have rendered such practical work so much more valuable and trustworthy that it may almost always now be relied on to furnish more or less adequate information. Nevertheless, the Krantz models of the curves of equal velocity are of great value in affording a graphic and concise review of the whole scheme of light vibration in the two great optical types of doubly refractive crystals.

For all practical purposes the isochromatic curves of equal retardation, currently known as the "rings round the optic axes" of crystals in convergent polarised light, and the isogyres, better known as the "dark cross" and the "hyperbolic brushes," are alone of prime and essential importance.

Given a tabular crystal perpendicular to the first median line, and as accessory apparatus to the microscope either the Miers stage goniometer, the Fedorov universal stage, or that of Klein, the observation of the interference figure, the localisation of the optic axes, and the measurement of their angle of separation, can be carried out without any serious difficulty. Also, even when tabular crystals are not available and sections are too difficult to prepare, if a liquid of the same refractive index as the mean of the crystal indices can be found by trial from among a number of available liquids without action on the substance, such as those the refractive indices of which are tabulated on pages 810 and 1185, the crystal apparently becoming invisible in such a liquid when the indices are matched, the optic axial angle can be measured with a whole crystal of other than tabular habit. But in more difficult cases, such as that of a crystal in a rock section, or one of a group not readily detachable, or a crystal too small for such manipulation, the optic axial angle can still be determined by the use of convergent light by the method of Becke, or by use of parallel light by the method of Fedorov.

Direct Determination of Optic Axial Angle by the Miers Stage Goniometer.—The Miers stage goniometer is very useful in all simpler cases, such as for measuring the optic axial angle of a miniature crystal of tabular form perpendicular to the acute bisectrix. The crystal is

mounted with wax or other cement [1] on the end of the holder-needle, so that the plane of the optic axes is perpendicular to the goniometer axis. The cross spider-lines of the eyepiece are to be arranged parallel and perpendicular respectively to the goniometer axis, and the directions of vibration of the Nicols at 45° to these directions. The convergent system and Bertrand lens being in position, the objective is brought down by the coarse adjustment as close to the section-plate as possible without impeding the free rotation of the needle and crystal. Even if this be not close enough, employing the $\frac{1}{4}$-inch objective so suitable for this work and both sub-stage condenser and stage lens as convergent system, to permit of a full field of interference curves being obtained, it will be adequate to show the central part of the field, where each optic axial hyperbolic brush is to be brought in turn to the cross-wires at the centre. When the crystal has been adjusted for symmetry of the figure to the centre, the rotation is effected first on one side and then on the other until the vertex of each brush in turn is delicately adjusted to the spider-line (that one which is parallel to the tangent to the brush at the vertex of the hyperbola), when a reading of the goniometer circle is taken. (See Fig. 681, page 923.) The difference of the readings for the two brushes is 2E, the apparent optic axial angle in air.

If the mean refractive index β has already been determined, the true angle $2V_a$ can at once be calculated by means of the formula :

$$\sin V_a = \frac{\sin E}{\beta}.$$

But when a second plate perpendicular to the obtuse bisectrix is available, measurements with both plates can be made in oil or a still more highly refractive liquid such as monobromonaphthalene, and the true angle calculated from the apparent acute and obtuse angles in the liquid, $2H_a$ and $2H_o$, just as described in Chapter XLVIII., with the aid of the formula :

$$\tan V_a = \frac{\sin H_a}{\sin H_o}.$$

The circular cell with truly parallel-surfaced plate-glass sides is used to contain the liquid ; it fits readily in the cut-away recess in the goniometer stage-plate, and when pushed as far as it will go in this recess, resting on the semicircular end, it is centrally placed. There is an opening in the cylindrical wall of the cell adequately large to admit the crystal, and the cell is arranged so that this opening is at the top when the microscope is arranged horizontally for this immersion work, as shown in Fig. 823. The goniometer is so constructed that when the cell is thus placed in position the crystal and needle-end will be completely immersed in the liquid, when the cell is three-quarters filled. Two such cells of different sizes are shown lying on the base-board in Fig. 822 ; the circular metallic basal annulus of each of these cells has the same radius as the semicircular end of the recess in the stage-plate.

[1] The particular cement chosen will depend on the nature of the highly refractive immersion liquid which is to be used in the later measurement of the true optic axial angle. It must obviously be a wax, gum, or cement which is not soluble in that liquid.

Even if there be only the one plate available, perpendicular to the acute bisectrix, the true angle can be found, as accurately as microscopic observation can ever go, by using as the immersion liquid one which has a refractive index for sodium light equal to the mean of the three refractive indices of the crystal, the observed angle being then the true angle $2V_a$ for sodium light and approximately so for other wave-lengths. If the refractive indices have not been determined it is sufficient for approximate work to choose a liquid in which the crystal becomes invisible, for the refractive indices are then approximately alike.

As the true optic axial angle $2V_a$, and even the apparent angle in air 2E, as well as the nature of the interference figure itself, are so highly characteristic of the crystals of a substance, this determination and the observations connected with it are of great importance as furnishing data for a valuable description of the substance, and when no crystals large enough for the preparation of section-plates for use with the optic-axial-angle goniometer described in Chapter XLVIII. are to be had (a crystal as large as a pin's head will often suffice, when the cutting-and-grinding goniometer described in Chapter XLIII. is available) the crystallographic microscope is the only resort, and proves of the utmost value. For results almost as accurate as those obtained with larger crystals and the specific measuring instruments referred to in Chapter XLVIII. can be attained by its careful use with microscopic crystals. For the simpler cases the Miers goniometer employed as just described is excellent, but for the more difficult cases recourse must be had to the universal stage, the various methods of using which will now be proceeded to.

Convergent light methods are available whenever at least one optic axis appears within the field of vision. The method requiring the use of the Becke drawing table shown in Fig. 839 (page 1166) in the previous chapter is generally applicable, and accurate to within five degrees. The method involving the use of the double-screw micrometer described by F. E. Wright,[1] in an excellent memoir on this subject of the new methods of microscopic investigation, and illustrated in Fig. 828 (page 1157) in the previous chapter, is also of general application and both more accurate and simpler. It is an up-to-date improvement on the older well-known procedure of Mallard, and utilises Wulff's method of projection. The results with both methods require to be plotted on a stereographic projection, and the optic axial angle is then measured graphically on the projection. Hutchinson's stereographic net of particularly convenient size, shown in Fig. 52, page 104, is extremely useful for the purpose ; or, if preferred, the net of either Fedorov or one of the other authors referred to in Chapter VI. may be used.

For parallel light work the method of Fedorov is the most satisfactory, provided the position of one optic axis can be determined directly. The situation of the second optic axis is then determined by the method of extinction curves.

The most accurate results by both parallel and convergent light methods are with sections through which both optic axes are visible,

[1] *Amer. Journ. of Science*, 1907, *24*, 317.

while if neither is to be seen none of them are really satisfactory, and the method just described of immersion in a liquid of the same refractive index is the only hopeful one.

Indirect Method of Mallard as improved by Wright.—As the Bertrand lens affords an image, the secondary one, of the interference figure in convergent polarised light, which can be focussed by a Ramsden micrometer positive eyepiece, a micrometer spider-line can be simultaneously focussed. It is only necessary, therefore, to employ a Ramsden micrometer such as that shown in Fig. 827, in order to be able to get a linear measurement of the distance between the two vertices of the hyperbolic brushes, when both are visible in the field of view. An engraved micrometer such as is given with the Groth universal apparatus, and likewise brought into the focus of the positive eyepiece, serves the same purpose somewhat more roughly.

The improvement introduced by Wright[1] consists in using a double-screw micrometer. It is an ordinary Ramsden micrometer with the addition of a second micrometer at right angles to the first, each micrometer having its own screw with divided drum, and its own movable spider-line following absolutely the movement of the screw, as recorded by the drum divisions and a scale of notches or " comb," every fifth notch deepened, to record the number of complete drum and screw revolutions. Its construction will be clear from Fig. 828, page 1157. The two movements are adjusted so that the two movable spider-lines are exactly perpendicular to each other. Each movement can be accurately read to 0·005 mm. The Ramsden positive eyepiece is fitted above with a cap pierced by a small aperture, the function of which is to act as a small stop to minimise any possible errors of parallax. The two co-ordinates of any point on the dark axial bar (isogyre) of an optic axis in the field of view may thus be taken directly, when once the angular calibration value for the movement of each of the two spider-lines has been determined, in the manner which will presently be explained. The angular values may then at once be transferred to a stereographic net and the rest of the procedure of Becke's method followed (described in the next section), which is essentially based on Mallard's principle and original suggestion, for the determination of the optic axial angle.

Mallard[2] represented the distance of the axis of the microscope from one of the brush-vertices by D, which is thus the lineal representative of E, half the apparent optic axial angle in air. He then showed that

$$D = K \sin E,$$

where K is a constant (the Mallard constant) for the particular optical lens system employed. The lens system must satisfy the well-known Abbe condition of aplanatism :

$$\frac{\sin u}{\sin u'} = \frac{n'A}{n} = \text{a constant},$$

[1] *Amer. Journ. of Science*, 1907, *24*, 336.
[2] *Bull. Soc. Min. Fr.*, 1882, *5*, 77.

in which u and u' are the angles of convergence of the rays in the two parts of the convergent systems of lenses, n and n' their indices of refraction, and A the magnification. All the microscopes by the best makers, supplied with condensing system, aplanatic objective such as a Swift $\frac{1}{4}$-inch or a Fuess No. 9 of equivalent focal length of 2·7 mm. and numerical aperture 0·97, Bertrand lens, and Ramsden eyepiece, fulfil these conditions. Moreover, Mallard showed that D is always proportional to the sine of the apparent half-angle E of the optic axes in air, as will be obvious from his formula. The constant K is determined experimentally, by means of a few section-plates perpendicular to the first median lines of crystals of well-ascertained magnitude of 2E, as varied as possible. We then have :

$$K = \frac{D}{\sin E}.$$

The simplest method is to measure with each of these chosen section-plates the distance between the vertices of the two dark hyperbolic brushes, as if measuring an optic axial angle but in scale and drum divisions instead of angular measure, this distance being 2D. That is, the movable spider-line undergoing calibration is adjusted first to the summit of one hyperbola and then, after noting the reading of the scale and drum, it is traversed by rotation of the milled head of the drum until the other hyperbolic summit is similarly adjusted, when another reading is taken. The difference of the two readings is 2D. As we know the actual angular value 2E of the optic axial angle in air thus linearly measured we can at once make up the equation for K above given and find K. Doing this for the several section-plates chosen, we obtain several more or less concordant values for K, the mean of which may be taken as the trustworthy value of the constant once for all. We are then in a position to employ Mallard's equation to find the E, and therefore 2E, of a crystal of unknown optic axial angle, by use of the double micrometer to measure linearly the distance between the vertices of the two hyperbolæ when the latter are both visible in the field of the microscope, for $\sin E = D/K$.

When the section-plate is not quite perpendicular to the bisectrix of the angle between the optic axes, the spider-line is placed over one axial vertex, the section rotated 180°, and the spider-line traversed to the new position of the same vertex ; half the difference between the two positions is a value of D corresponding to the real distance of the optic axis from the centre of the field. A similar operation is then performed for the other hyperbolic vertex, and a value of D obtained for this corresponding to the distance of this second vertex from the centre. By using the formula $\sin u = D/K$ to calculate u in each case, two values of u are obtained corresponding to the real angles made by each optic axis with the normal to the plate, the sum of the two being 2E.

Method of Becke, by use of the Drawing Table.—When the plate is not nearly perpendicular to the acute bisectrix of the optic axial angle the method in its simple form is inapplicable. But Becke (references

given at foot of page 1202) has admirably generalised it by the introduction of his drawing table and the use in connection with it of the stereographic net. The drawing table, however, is not absolutely indispensable when the microscope is fitted with the Dick arrangement, described so fully in the last chapter, for the simultaneous rotation of both Nicols, which was first arranged for Mr. Allan Dick by Swift and has now also been adopted by Fuess and other first-class makers of crystallographic microscopes. Becke's method depends essentially on the fact that the isogyres, the dark hyperbolic brushes, pivot round the poles of the optic axes when the section-plate is rotated in its own plane on the stage of the microscope. The position of one optic axis, which should be visible in the field for the method to be applicable in its more accurate form, is determined by the intersection of the isogyres observed about this axis for different positions of the stage, some definite angular distance apart, such as 30° or 45°. For this purpose he projects the interference figure by means of the Abbe camera lucida (shown in Fig. 839 in the previous chapter) on his rotatable drawing table (also shown in Fig. 839), which can be accurately centred by three screws arranged at intervals of 120°, or by two screws arranged at 90°. That is to say, simultaneous images of the interference figure and the drawing on the drawing table are arranged to be obtained on looking through the camera lucida. The rotating plate of the drawing table has a series of concentric circles engraved on it to facilitate rapid centring to identity of axis of rotation with that of the centre of the image of the interference figure. The drawing table is graduated in degrees, and may, if desired, be supported on an arm attached to the microscope stand instead of on the base-board, and is recommended to be so used by Wright.

Having fixed its position so that its axis of revolution coincides after reflection in the camera lucida with the optical axis of the microscope and so that it is also at the proper distance from the eye for clear vision, and having determined its constant K corresponding to the K of the microscope in the formula $D = K \sin E$ (several methods of determining which are given by Becke, analogous to that used for the Ramsden or Wright micrometer just described), any interference figure can be traced and the angular position—the polar angle ρ and longitude angle ϕ—of any point in the projection can be determined from the drawing and plotted subsequently on a stereographic projection net, such as that of Hutchinson given in Fig. 52. Thus the angular distance between any two points, for instance the two optic axes if both are present at once in the field, can be graphically found. As stated in the last section, however, this particular simple problem can be solved more readily by the use of Wright's double micrometer, the drawing table being unnecessary. The value of the method comes in when only one optic axis is present in the field of view.

When only one optic axis is visible, the method of Becke depends on the fact that the dark axial bar or hyperbolic brush, the isogyre, exhibits a curvature definitely related to the magnitude of the optic axial angle, and also on the well-known Biot-Fresnel rule explained on page 897

in Chapter XLII. This important rule, which Biot [1] demonstrated experimentally and Fresnel [2] explained theoretically, is that **the directions of extinction in any section of a biaxial crystal are parallel to the traces, on that section, of the planes bisecting the angles between the two planes containing the normal to the section and the optic axes.** The normal to the plate being the common line of intersection of all four of these planes, and the two bisecting planes being at right angles to each other, their traces, the extinction directions of the plate, are also at right angles to one another. They (the extinction directions) are the directions of possible light vibration in the plate, those of the two rays into which by virtue of the property of double refraction the light is divided on entering the crystal plate. They are also the principal axes of the elliptic section of the optical indicatrix made by the plate. This law of Biot and Fresnel is a natural extension to biaxial crystals of the law of Malus [3] governing the case of a uniaxial crystal, that **the lines of extinction in any given section are parallel and perpendicular respectively to the trace of the plane containing the normal to the section and the optic axis.**

This fundamentally important Biot-Fresnel law can be illustrated by a very simple model, of which the essentials are (1) a flat board to represent the crystal plate, (2) a rod standing upright from the centre to represent the normal, (3) two other rods to represent the optic axes, each hinged at one end with a ball-and-socket joint to the centre of the base-board, from which they thus spring in common with the fixed rod, but are able to be fixed at any required angle to each other, the optic axial angle, and to the fixed normal rod, and (4) a sheet of metal with one essential edge truly straight. On laying the metal sheet against the normal rod and one of the optic axial rods, with the straight edge resting as a ruler on the base-board, the trace of the plane on the base-board, or preferably on a card cut to the shape of the crystal plate resting on the base-board, can be drawn by ruling. Similarly the trace of the plane of the normal and the other optic axis can be drawn. On then bisecting the two angles, acute and obtuse, formed by these two lines thus drawn, the two rectangular extinction-vibration directions are obtained, the traces of the two bisecting planes. When the card representing the crystal section has been accurately cut, the relations of the extinction directions to the faces bounding the section are thus at once seen.

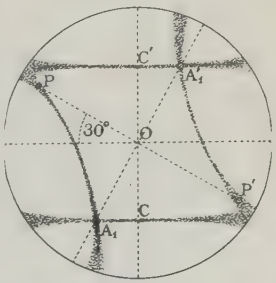


FIG. 854.

The axial bar is first drawn when in a position parallel to the horizontal cross-wire, that is, when the extinction directions of the section are parallel to the vibration directions of the Nicols, as shown at A_1C in Fig. 854, which is due to Wright. The graduation of the circle of the drawing table for this position should also be made the same as

[1] *Mém. de l'Acad. de l'Inst. de France*, 1820, *3*, 228.
[2] *Pogg. Ann.*, 1831, *23*, 542.
[3] *Mém. prés. à l'Inst. Sc. math. et phys.*, 1811, *2*, 303.

that of the rotating stage of the microscope. This line A_1C is the trace of the optic axial plane. The microscope stage or the Nicols and the drawing table are then revolved either 30° or 45° in the same direction, and the axial bar is drawn in the new position A_1P; A_1 is common to both, as it is the position of the optic axis about which the brush is rotated, that is, it is the pole of the optic axis. The drawings are then repeated after revolution of the microscope stage (or the Nicols) or drawing table alone through 180°, giving A'_1C' and A'_1P', in order to determine the exact centre of the field O. For the centre is the middle of the line joining the poles in the two positions 180° apart. The angle u which this optic axis A_1 makes with the normal to the plate satisfies Mallard's equation $D = K \sin u$, in which D is the distance on the drawing of the pole A_1 from the centre of the field O, and K is the usual constant for the apparatus. If both axes were visible we should simply proceed likewise to find the position u' of the pole of the other axis, from the equation $D' = K \sin u'$, as shown in the last section. Then $u + u' = 2E$. When the plate is perpendicular to the acute bisectrix $u = E$.

But only one axis being visible we proceed as follows. The point P being on the dark isogyre, the plane of vibration of the light waves propagated at this point is the same as that of the polarising Nicol. It is, therefore, only necessary to apply the law of Biot graphically in order to find the second optic axis A_2. The graphical operations necessary thus to measure the optic axial angle A_1A_2 from the data on the drawing are developed in Fig. 855, which is also due to Wright. The points A_1 and P are first accurately located in the drawing, reduced to angular values by use of the Mallard equation, and then plotted on a stereographic projection-net printed on tracing paper, such as that of Hutchinson given in Fig. 52. The great circle $A'_1A'_2$ to which P is polar, and the horizontal great circle A_1A_2 passing through the known point A_1, are then drawn. The point A'_1 is then the intersection of the great circle passing through P and A_1 with the great circle $A'_1A'_2$, and the line OC is the trace of the plane of vibration of the polarising Nicol as it occurs after rotation for the 30° or 45°. As A'_2C is equal to A'_1C by definition and the conditions of the drawing of the axial isogyre, and the intersection A_2 of the great circle PA'_2 with the great circle A_1A_2 determines A_2, A_1A_2 is the desired optic axial angle.

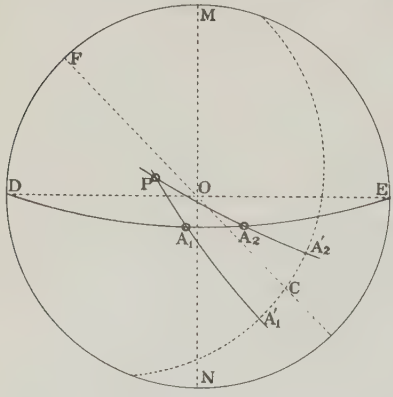


FIG. 855.

This concrete illustration will, it is hoped, give a clear idea of the method of Becke in applying still further the principle of Mallard, and of the use of the drawing table and stereographic net. Becke has also

described methods in which the graphical constructions are performed on gnomonic and orthogonal projection-nets, but the stereographic net is both equally adequate and on the whole more satisfactory, having such definite relations to the optical ellipsoid and to the crystal structure.

Collingridge's Alternative Method.—The following valuable contribution to this important subject, which will help materially to render it clear, is taken from a "Note on the Determination of the Optic Axial Angle of a Crystal in Thin-section by the Mallard-Becke Method," by Harvey Collingridge.[1]

"Mallard's original method[2] was based on the measurement of the linear distance, as determined by an eyepiece-micrometer, between the optic axes in a section of the crystal at right angles to the acute bisectrix viewed in convergent light.

"Professor F. Becke improved on this method by utilising sections which were not at right angles to the acute bisectrix, but in which both optic axes were visible in the field. He projected both axes by means of an Abbe camera-lucida on to a revolving drawing-table, and by means of the Mallard equation plotted the axes on a stereographic projection and thus obtained the optic axial angle, the angles of course being corrected for refraction to the true angles in the crystal section. Professor Becke[3] subsequently, by utilising the Biot-Fresnel law, formulated a graphic method of obtaining the optic axial angle from a section in which only one axis was visible.

"As a controversy has arisen between Professor Becke and Dr. F. E. Wright as to the correct method of obtaining the position of the second axis, and as the method the author proposes seems to avoid the debatable point, a brief résumé is given below.

"Professor Becke's method is as follows (Fig. 856):

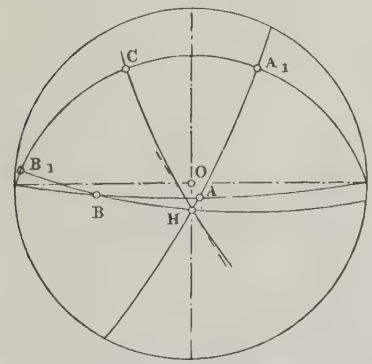


FIG. 856.—Becke's Method.

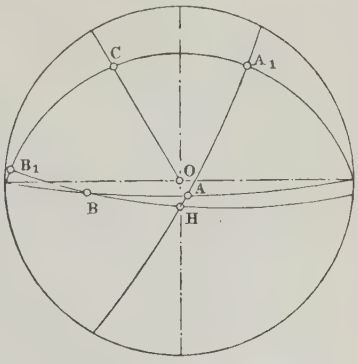


FIG. 857.—Wright's Method.

"The visible isogyre is first drawn when it forms a straight line in an

[1] *Mineralogical Magazine*, 1913, *16*, 348.
[2] E. Mallard, *Bull. Soc. minéralog. de France*, 1882, *5*, 77.
[3] F. Becke, *Min. Petr. Mitt.* (Tschermak), 1905, *24*, 1. See also J. W. Evans, *Mineralogical Magazine*, 1907, *14*, 230 and 276.

east and west direction, thus determining the optic axial plane. The section is then turned through any convenient angle, say 30° to 45°, and the drawing-table is revolved the same amount in the same direction. The new position of the isogyre is then drawn. The intersection of the two traces of the isogyre gives the position of the visible optic axis A. Any convenient point H on the second position of the isogyre is taken and with A is transferred, duly corrected for refraction, to a stereographic projection. A great circle through A on an east and west diameter is drawn, thus marking the optic axial plane, and on which consequently the second optic axis must lie. A great circle HAA_1 is drawn through H and A. Another great circle A_1CB_1, of which H is the pole, is drawn cutting HAA_1 in A_1. The plane of vibration through H is then given by a great circle tangent at H to a straight line parallel to the second position of the plane of vibration through the lower nicol. This intersects the great circle A_1CB_1 in C. On this great circle A_1CB_1 an arc CB_1 is set off equal to the arc CA_1. A great circle HBB_1 is then drawn cutting the great circle which marks the optic axial plane in B. By virtue of the Biot-Fresnel law, the optic axial angle 2V is then read directly by the arc AB.

" Dr. Wright, in his recent book on *The Methods of Petrographic-Microscopic Research*,[1] takes exception to Professor Becke's method of finding the plane of vibration through the point H, and is of opinion that it is more correctly represented by the great circle passing through H and the intersection C of the polar great circle with the trace of the principal plane of the lower nicol (Fig. 857).

" The author proposes to avoid this contentious point by the following simple method (Fig. 858):

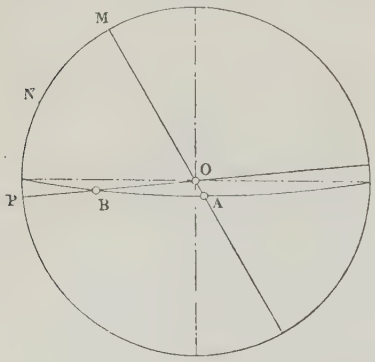


FIG. 858.

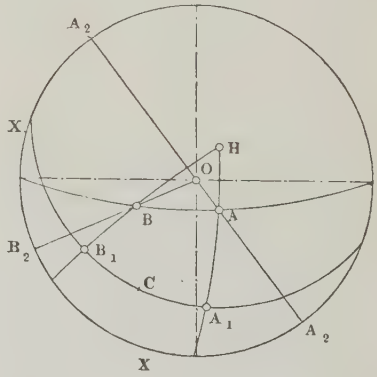


FIG. 859.

Collingridge's Method.

" Instead of taking a point H on the isogyre the centre of the field O is used. A straight line is drawn from O through the first optic axis A, cutting the circumference of the stereographic circle in M. The position of extinction N is then marked on the circumference of the same circle.

[1] F. E. Wright, Carnegie Institution of Washington, 1911, Publ. N . 158, p. 160.

From N an arc NP is set off equal to MN. P is then joined to O by a straight line and produced if necessary to cut the great circle marking the optic axial plane in B. The point B will then be the second optic axis.

"The advantages that this method would appear to give are the following:

(1) All doubt is removed as to the correct plane of vibration through H.
(2) Greater ease and accuracy in graphic construction as—
    (*a*) O may be determined with far greater certainty than a point on a more or less clear isogyre.
    (*b*) Only one great circle is necessary to be drawn, the remaining lines being straight.
    (*c*) The line of extinction can be found with considerable accuracy in convergent or parallel light, the latter being no doubt the better.

"The method proposed is of no service when the axial plane lies on a diameter, as the line of extinction will then be coincident with it.

"It frequently happens that, when the optic axial angle of a thin section or cleavage flake of a crystal is required, an optic axis is a little way beyond the field, thus rendering the determination by the Mallard-Becke method impossible. In such a case it is possible to make a fairly good determination by combining Professor Becke's method of obtaining the second optic axis with the method proposed above by the writer (Fig. 859). As in Professor Becke's method the optic axial plane is found by placing the isogyre horizontally in an east and west direction. The point H is then fixed precisely as before, and in addition the position of extinction is noted. All these data are transferred, duly corrected for refraction, to a stereographic projection. On this stereographic projection the point C on the great circle polar to H and the position of extinction X on the base circle are marked. Now if A and B be the positions of the optic axes, it is clear, by virtue of the Biot-Fresnel law, that OX will bisect the angle BOA (internally or externally), and also if B_1 and A_1 be the points where great circles HB and HA cut the great circle polar to H, that $CB_1 = CA_1$. We now proceed to find the points A and B by trial and error. Set off on the base circle a series of equal arcs XA_2, XB_2, and on the polar great circle a series of equal arcs CA_1, CB_1. Trial and error will then determine with a reasonable amount of accuracy which values of A_2, B_2, A_1, and B_1 are to be taken so as to fulfil the necessary condition that OB_2 and HB_1 intersect at B, while OA_2 and HA_1 intersect at A. The procedure need not necessarily be a long one, as inspection of the field gives a rough idea of where the optic axis A is situated.

"It is not suggested that the method can compare in accuracy with the case in which one optic axis is visible, but it is claimed that fairly reasonable accuracy may be obtained if no other method can be used. The diagram (Fig. 859) is that for a cleavage flake of labradorite. 2V was found equal to 69°. By using a very wide angle condenser, and thus rendering both axes visible, 2V was determined as 71°."

Method of Fedorov, by Use of the Universal Stage.—Sections of crystals which would formerly have been considered quite hopeless for the purpose can now be made to yield the optical constants with very fair approximation to the truth by this method. Parallel polarised light is chiefly used by Fedorov (references given on page 1160), with the crystal mounted on the universal stage, which is fixed on the ordinary stage of the microscope in the manner described in the previous chapter.

The essence of the method is that when an optic axis is brought parallel to the axis of the microscope in parallel plane-polarised light the section-plate remains uniformly dark when revolved about that axis. The universal stage enables the optic axis to be thus brought parallel to the microscope axis with great ease and consequently to be found directly by experiment, when the optic axis in question emerges somewhere in the field of view. The positions of both optic axes are found in this way in parallel light if possible, but if the optic axes do not emerge they are found by means of determinations of extinction directions in definite zones of faces; the results are plotted on a stereographic net, with the aid of a second such net on tracing paper. It is then possible to determine graphically both the optic axial angle and the orientation of the section-plate with respect to the optical ellipsoid, although neither optic axis may be visible through the plate. The true angles in the crystal are found before plotting on the net, by use of the mean refractive index β of the crystals, which Fedorov also gives a method of finding, together with the approximate double refraction. The Biot-Fresnel rule is again much used as a base of operations, namely, that the planes of vibration of light waves propagated in any given direction bisect the angles between the two planes each containing one of the two optic axes and the given direction. Fedorov recommends the use of circular glass mounts 2 centimetres in diameter for the crystals or mineral sections, instead of the ordinary microscope 3-by-1-inch slips. The universal stage enables a crystal section to be examined under the microscope in any position, and to be revolved about any axis, thus affording control over all possible orientations.

There are four cases distinguished by Fedorov, for which he recommends certain procedure as most convenient: (1) when both optic axes are visible, and inclined between 15° and 55° to the normal to the section; (2) when one optic axis only is visible, and inclined less than 20° to the normal to the section, the second optic axis being unable to be brought into view by any revolution of the stage; (3) the same as (2) but the inclination of the optic axis is more than 20° to the normal; (4) both optic axes are outside the field of view of the microscope. The methods recommended for treating these four cases are briefly as follows.

(1) The positions of the two optic axes are determined by bringing each one, by means of the two circles V_1 and H_1 of the universal stage as shown in Fig. 834 (p. 1161), into the vertical position, when the crystal will remain dark under crossed Nicols during the whole revolution of the microscope stage or when the Nicols are simultaneously rotated. Also in feebly convergent light the optic axis can actually be seen, when

so adjusted, in the centre of the field. The position of each is then confirmed by means of extinction angles along definite directions, and by plotting the results on a stereographic projection ; the " optical curves " thus obtained will all intersect in the optic axis in question.

To obtain such an optical curve the crossed Nicols are first placed in some definite position, then H_1 is turned through 5° at a time and for each position the angle of inclination about V_1 is found for which the crystal plate is at maximum darkness. The observed angles are then reduced to true directions in the crystal by use of the mean refractive index β of the crystal, and those directions in the crystal are found for which the extinction is 0° for a given position of the Nicols. The curve uniting these directions is the " optical curve " of Fedorov. Other analogous curves are then obtained and plotted for other definite positions of the crossed Nicols, when they will all be found to intersect in the optic axis. In the case (1) before us, as the position of the latter has been found approximately already, only one setting of H_1 at 5° or 10° on each side of the approximately known position is necessary. Convenient positions of the Nicols are at 0°, 45°, 15°, and 30° from the axis of V_1.

When both axes are present in the field of view their positions are determined each separately as above, and plotted in stereographic projection ; then the optic axial angle $2V_a$ is measured graphically, with the aid of the formula :

$$2V_a = \cos v \,.\, \cos v' + \sin v \,.\, \sin v' \,.\, \cos (h - h'),$$

in which v and v' are the readings on the vertical circle V_1, of the universal stage, for the two respective optic axes, and h and h' the corresponding readings on the circle of the rotating microscope stage.

(2) The section-plate being nearly perpendicular to an optic axis (within 20°), the universal stage is arranged with the two gimbal circles H_1 and H_2 horizontal. H_2 is then turned slightly about its axis of rotation A_4, and also inclined about V_2 by rotation about axis A_3, until darkness is produced and the optic axis coincides exactly with the axis of the microscope. To find the other optic axis, the vertical goniometer circle V_1 and the gimbal circle H_1 are then rotated until darkness is again attained, the plane of the optic axes being thus found, and also the apparent position of the axis β of the optical ellipsoid. The circle H_2 is then brought back to 0° with respect to circle V_2, and H_1 is rotated until the visible optic axis (A_1 in Fig. 860) comes to lie in the plane (OCD in Fig. 860) which is perpendicular to the axis A_1 of V_1 and the extinction curve determined, the intersection of which with the plane of the optic axes in the projection fixes the position of the second optic axis.

To determine this extinction curve the extinction angle EOD in Fig. 860 is first found, when the stage is in the horizontal position, and also subsequently when it is at such an inclination about V_1 that the extinction angle is 45°. This can be recognised by placing the Nicols in the 45° position and then revolving about V_1 until darkness ensues. By thus ascertaining the angle of revolution necessary to attain the required 45° extinction angle, the great circle CA_2M (the plane in which the unknown optic axis must lie when the extinction angle is 45°) is fixed with reference to the horizontal diameter. The position of A_2, the second optic axis, on CA_2M is at the point where it is intersected by a radius OB drawn at an angle DOB equal to twice the extinction angle DOE.

The results can be confirmed by determining the positions of the axes α and γ of the optical indicatrix both from the projection and directly by observation. They may also be checked by determining the extinction curve for revolution about the circle V_2.

Owing to the effects of elliptical polarisation in producing indistinctness of extinction phenomena when the section-plate is steeply inclined, the above simple method does not always work perfectly, in which case another more general one is

available. After having placed the known optic axis A_1 in the plane (NO in Fig. 861) normal to the axis of the circle V_1, as in the method just described, the extinction angles are measured for different inclinations of the stage about the axis of V_1 (MOE in Fig. 861 being that for the horizontal position), and reducing these angles as usual to real angles within the crystal by means of its average refractive index ; the reduced angles are then plotted on a stereographic net, as in Fig. 861. The radii which make an angle with the vertical diameter NOM equal to twice the extinction angles (OA_2 in Fig. 861 is such if EOA_2 be drawn equal to EOM) will be planes containing the second optic axis A_2, the exact location of which can be found by noting for two given radii, such as OA_2 and OA'_2 (MOE′ being a new extinction angle and $E'OA'_2$ its equal, drawn in by construction), the small circle the arc $A_2A'_2$ of which intercepted is equal to the angle of revolution of the stage. The determinations should be repeated for different stage inclinations, such as those equivalent to 0°, 10°, 20°, 30°, 40°, and 45° within the crystal, on both sides of the normal to the section-plate. This method is perfectly general, and the result can be checked by drawing the great circle CF, which marks the position which the plane OA'_2 would assume were the section-plate turned back to

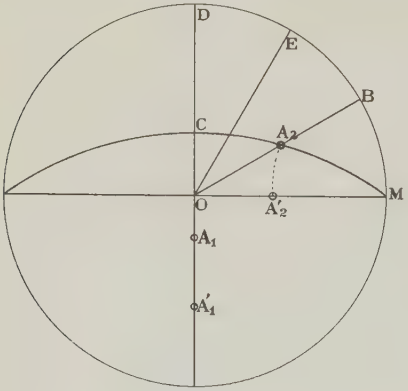


FIG. 860.

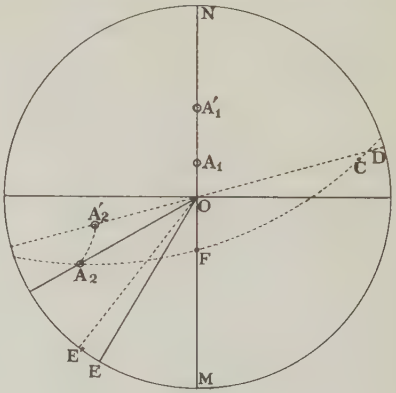


FIG. 861.

its original position. In practice the position of A_2 is determined for a number of different angles of revolution about the goniometer axis of the circle V_1 and the mean taken as the true situation of A_2.

(3) When one optic axis is visible, inclined between 20° and 55° within the crystal to the normal to the section-plate, the second optic axis being out of sight, the visible optic axis is first determined by optical curves as before, and the second optic axis by means of extinction curves about the axes of rotation both of the main goniometer circle V_1 and of the arc V_2. The results may be confirmed by determinations of the positions of the three axes of the optical ellipsoid α, β, and γ.

(4) When both optic axes are invisible their location is accomplished entirely by means of extinction curves, and the accuracy is of a low order, as a small error in the determination of an extinction angle affects the optic axial angle very considerably.

The above examples will have afforded some idea of the very valuable work of Fedorov, in devising methods of determining the optical constants with a single miniature section-plate of a crystal orientated anyhow, or a minute crystal of tabular form. In these methods, together with the method of Becke, and the simplification of the latter by the introduction of the principle of simultaneous rotation of the Nicols in crystallographic

microscopes, which we owe to the ingenuity of Mr. Allan Dick, as well as the modification of the Becke method introduced by Wright, dependent on the use of a double micrometer, crystallographers have now the means of investigating with considerable prospect of success crystals of minute size, possibly only thin miniature plates, which at first sight look most unpromising. The united labours of these workers have conferred an altogether higher value on the crystallographic microscope as an instrument of original investigation, quite apart from its magnificent and unique value in the study of the natural crystals in thin sections of rocks, to which crystals these methods are equally applicable.

Wright has made an interesting calculation of the probable frequency with which a crystal showing at least one optic axis may be encountered in a rock-section, and finds it to be 4 out of 10 in the case of uniaxial

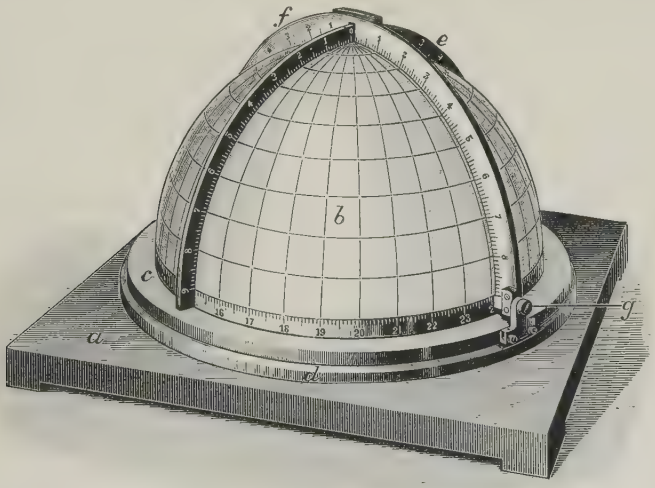


FIG. 862.—Nikitin's Hemisphere for the Graphical Solution of Universal Stage Problems.

crystals, and as high as 8 out of 10 in the case of biaxial crystals. As in all these cases results are certain to follow the careful application of these improved methods, it will be obvious that suitable individual crystal-sections for the measurement of the optic axial angle and other optical constants are likely to be found for such an investigation in every rock-section exhibiting clear crystals.

Nikitin's Hemisphere for recording Universal Stage Results.—A very useful apparatus, which is shown in Fig. 862, has been devised by W. Nikitin[1] in Fedorov's laboratory in Petrograd, for the purpose of graphically recording in pencil on the surface of a porcelain hemisphere the results obtained with the universal stage. A massive wooden base *a* carries the hemisphere *b*, the equatorial plane of which is circumscribed by a fixed metallic annulus divided directly into degrees. Vertical

[1] *Zeitschrift für Krystallographie*, 1910, *47*, 379.

great circles like meridians of longitude, and small circles resembling parallels of latitude, are clearly painted on the hemisphere at every 10°. The hemisphere is directly mounted on the circular plate *c* fixed to the base-board, and around it there revolves an outer annulus *d*, which carries with it two semicircular divided metallic limbs *e* and *f*; the former *e* is fixed in the vertical plane, so as always to follow a meridian of longitude, while the latter *f* is attached by hinges *g*, so that it can be inclined on either side, to reproduce the effect of the rotation of the inner gimbal of the universal stage, the inclination to the horizontal plane being measured by the limb *e*. This tilting limb *f* enables not only the angle between any two points on the sphere to be measured directly, but also any section of the sphere by any diametral plane to be traced on the porcelain surface by the pencil. As all symmetry planes of the optical ellipsoid are diametral, their traces can be at once drawn on the sphere. The positions of the optic axes can also be laid down on the sphere from the readings of the universal stage, and the optic axial angle can consequently be immediately read off between the two points thus marked with the aid of the hinged limb. The apparatus is also generally useful for the graphical solution of any stereographical problem which may arise.

Plotting spheres have also been described, with illustrations, by C. H. Warren[1] and by J. M. Blake,[2] which serve similar purposes to those for which the Nikitin hemisphere has proved so useful.

[1] *Amer. Journ. of Science*, 1917, *42*, 493.
[2] *Ibid.*, 1917, *43*, 237.

PART IV

CRYSTAL CHEMISTRY, DEFORMATIONAL PHYSICS AND ITS INTERFEROMETRY

CHAPTER LIV

ISOMORPHISM

Probably no scientific term has ever been so misapplied, so loosely applied, and indeed so often completely misunderstood, as "isomorphism." The term was introduced by Mitscherlich[1] in the year 1819, while in Stockholm with Berzelius, and at the latter's suggestion that a name should be given to the phenomenon which had just been observed by Mitscherlich during the course of his first research, namely, that certain salts of analogous chemical constitution—the phosphates and arsenates of potassium and ammonium, and also the metallic sulphates known as "vitriols"—crystallise in similar forms, in crystals which were indistinguishable with the goniometrical means then available to him. His exact words in the memoir on the phosphates and arsenates, which he read to the Berlin Academy in December 1819, are: "Ihre Formen so übereinstimmend sind, an Wert und Anzahl der Flächen und Winkel, dass es nicht möglich ist, irgend eine Verschiedenheit, selbst nicht einmal in den Charakteren, die zufällig scheinen, aufzufinden." He derived the word isomorphism from ἰσός, "equal to," and μορφή, "shape" or "form," so that the word means "equally shaped" or "identically formed."

It should not be forgotten, however, that Wollaston had already in the year 1812 discovered the phenomenon, as the result of accurate goniometrical measurements carried out with the reflecting goniometer which he had invented in 1809; he measured the crystals of the rhombohedral carbonates calcite $CaCO_3$, magnesite $MgCO_3$, chalybite $FeCO_3$, calamine $ZnCO_3$, and rhodochrosite $MnCO_3$, and also those of two orthorhombic isomorphous groups of minerals, namely witherite, strontianite, and cerussite (the carbonates of barium, strontium, and lead), and barytes, celestite, and anglesite (the sulphates of the same three metals). Wollaston, moreover, had perceived the true nature of the phenomenon, namely, that the crystal angles of the members of each series were only similar, not identical, and later he completed the study of the first group by measuring also the crystals of aragonite, the rhombic form of calcium carbonate. As has so often happened with British discoveries, however, Wollaston's observations were ignored until they were confirmed on the Continent by Mitscherlich, and adequate credit has never been given to Wollaston, the real discoverer of isomorphism.

[1] *Ann. Chim. Phys.*, 1820, *14*, 172; and 1821, *19*, 350.

Mitscherlich's further work in the years 1819 and 1820 with the vitriols, the sulphates of ferrous iron, copper, zinc, magnesium, nickel, cobalt, and manganese, moreover, had resulted in finding that not only were most of these salts isomorphous, but that, as regards five or six of them, each was capable of crystallising in either of two different forms, rhombic and monoclinic, and was thus "isodimorphous." The rhombic group, under ordinary circumstances, consists of magnesium sulphate (Epsom salts) $MgSO_4 . 7H_2O$, zinc sulphate $ZnSO_4 . 7H_2O$, and nickel sulphate $NiSO_4 . 7H_2O$; and the monoclinic group, as crystallised at ordinary temperatures, consists of ferrous sulphate $FeSO_4 . 7H_2O$, and cobalt sulphate $CoSO_4 . 7H_2O$. Although the two other members of the group, the sulphates of copper and manganese, usually crystallise in a third triclinic form with five molecules of water of crystallisation, as $CuSO_4 . 5H_2O$ and $MnSO_4 . 5H_2O$, Mitscherlich found that if the crystallisation were conducted at a temperature lower than 7° C. in the case of manganese sulphate rhombic crystals of $MnSO_4 . 7H_2O$ were deposited resembling those of Epsom salts. Further, if a crystal of either the rhombic or monoclinic group were dropped into a saturated solution of a member of the other group, this latter salt would crystallise out in the form of the crystal introduced. This evidence of dimorphism was further confirmed by Mitscherlich during the same year by the definite establishment of the much-discussed case of carbonate of lime, which occurs as the well-known trigonal (rhombohedral) calcite and the rhombic aragonite, as one of dimorphism. Somewhat later, in the year 1823, Mitscherlich discovered the very clear case of dimorphism of sulphur, and showed that the ordinary rhombic form could be converted into the monoclinic form by merely fusing and allowing partially to solidify (until a crust is formed), and then decanting the remaining liquid, leaving the monoclinic needles radiating from the sides of the crucible.

It is also interesting to record that Mitscherlich completed his first year's work by the first preparation of the potassium members of the large and important isomorphous series of monoclinic double sulphates crystallising with $6H_2O$, by mixing a solution of potassium sulphate with a solution of any one of the seven sulphates (then known as "vitriols") above referred to. Moreover, in the year 1827 Mitscherlich made the first preparation of selenic acid H_2SeO_4, the element selenium [1] having been discovered ten years previously by Berzelius; and he showed that the selenates derived from the acid are isomorphous with the sulphates, and that the series of double selenates prepared from it are isomorphous with the double sulphates, both crystallising with $6H_2O$, the whole, in fact, forming one single series $K'_2M''\left(\begin{matrix}S\\Se\end{matrix}O_4\right)_2 . 6H_2O$, just as the simple rhombic sulphates and selenates may be considered as one single series $K'_2\begin{matrix}S\\Se\end{matrix}O_4$. It was this discovery of these two important series which has rendered the many years of work possible which the

[1] So named from σελήνη, "the moon," on account of its relationship to the previously discovered tellurium (*tellus*, the earth).

author has devoted to their study and very detailed measurement. Even this was not all Mitscherlich's great service, for he was able subsequently to show that the chromates and manganates are isomorphous with the sulphates and selenates, and that the perchlorates and permanganates also form another orthorhombic isomorphous series; K_2SO_4, K_2SeO_4, K_2CrO_4, and K_2MnO_4 will be observed to be analogously constituted as regards the number of atoms present in the molecule, as are also $KClO_4$ and $KMnO_4$.

The first result of this magnificent work of Mitscherlich was to enable Berzelius, by making use of the principle of isomorphism, to fix with certainty the atomic weights of copper, cadmium, zinc, nickel, cobalt, iron, manganese, chromium, sulphur, selenium, and chlorine, the positions which he assigned to these elements being those accepted to-day; only the decimal places of their atomic weights have required correction as more accurate analytical methods and more delicate balances became available.

When Mitscherlich first bestowed the name isomorphism on the important phenomenon which he had discovered, he was not in possession of a goniometer delicate enough to detect the minute angular differences which exist between the crystals of similar symmetry of the substances which he classed as isomorphous, and which belonged to the tetragonal, rhombic, and monoclinic systems. There can be no doubt that from the broad point of view which was alone possible to him he did really believe in these early days that the crystals were "equal-shaped." But later, after the completion of his work on the selenates and the large series of double sulphates and selenates, and in view of the accurate measurements of Wollaston, he began clearly to doubt his earlier impression that literal identity of form occurred in the cases of these numerous isomorphous substances. For he caused to be constructed, by the then famous mathematical mechanician Pistor, the most accurate Wollaston goniometer which had up to that time been produced; it read to ten seconds of arc with the aid of four verniers. Instead, however, of employing it for its designed purpose, the carrying out of careful comparative angular measurements of great refinement, he used this super-delicate instrument for a research on the alteration of the crystal angles by rise of temperature, and never subsequently found an opportunity of returning to his originally contemplated task. This task it has fallen to the lot of the author to undertake, and during thirty years to carry out, with these two most important and extensive series of the isomorphous salts discovered by Mitscherlich. For the subsequent discovery by Bunsen in the years 1860 and 1861 of the two rarer alkali metals rubidium (1861)[1] and cæsium (1860),[2] belonging strictly to the same family group as potassium, at once trebled the number of salts composing those series, and the K in the two general formulæ given on the previous page may be replaced by the general letter

[1] So called by Bunsen from *rubidus*, Latin for "darkest red," on account of its deep red spectrum line.

[2] From *caesius*, Latin for the blue colour of the sky, because of its two brilliant sky-blue spectrum lines.

R, standing for any one of these three alkali metals. It also stands for the radicle base ammonium NH_4, which has the singular property of replacing the alkali metals without change of the type of symmetry; and also for the metal thallium,[1] which was discovered by Sir William Crookes in the year 1861.

The last definition of isomorphism which we have direct from Mitscherlich was: "Substances possessing an analogous composition, which crystallise in the same form (or in similar forms), and which are capable of mixing in all proportions, are isomorphous." Even this definition will be shown to be inadequate, for two of the most perfectly isomorphous substances, for instance, potassium and cæsium sulphates K_2SO_4 and Cs_2SO_4, will not form mixed crystals, the reason for which is now thoroughly understood and will be gone into fully presently; in passing it may be stated that this reason is too great a difference in the dimensions of the unit cells of the two similar space-lattice structures.

Rigidly, employing the term in the strictest sense originally intended by Mitscherlich and with due regard to the derivation of the word, there is only one class of isomorphous crystalline substances, namely, those crystallising in the forms of the cubic system. For by reason of the very high degree of symmetry, the angles of all the forms of the cubic system are fixed by that symmetry; even where the angles between the various faces are not 90°, 60°, 45°, or 30°, they are still of definitely fixed value, and their actual values, correct to a minute of arc, have been stated in Chapter X. in describing the forms of the cubic system. The isomorphous substances belonging to the other six systems of symmetry should, therefore, strictly speaking, be termed "homœomorphous" (similar-shaped) rather than isomorphous. The latter term has come into general use, however, and may be retained with advantage, provided its true meaning be thoroughly understood. It must be remembered also in connection with cubic substances that while it would be correct, for instance, to describe all the members of the large family of alums, $R'\,R'''\left(\begin{matrix}S\\Se\end{matrix}O_4\right)_2 . 12H_2O$, as isomorphous, in the sense undoubtedly intended by Mitscherlich, in that they are of similar crystalline form and analogous chemical constitution, yet it would not be correct to describe the alums as isomorphous with iron pyrites, for instance, a substance of totally different chemical constitution FeS_2, although it crystallises not only in the same system of symmetry, the cubic, as the alums, but also in the same class, 30, of that system, and the angles between the analogous faces of the alums and pyrites are absolutely identical. The two cases do not even fall in with the view of Mitscherlich—that isomorphism depends on a similar number of atoms being present in the molecules of the two compounds; for while iron pyrites is a simple binary compound, with only three atoms in the molecule, the alums are complicated substances composed of a large number of atoms, no less than 48 even when the simpler half-formula is employed rather than the constitutional formula exhibiting their

[1] So named by Sir William Crookes from θαλλός, "a green twig or bud," by reason of its bright green spectrum line.

derivation as double sulphates and selenates with water of crystallisation, $R_2'\left(\begin{matrix}S\\Se\end{matrix}O_4\right) . R_2'''\left(\begin{matrix}S\\Se\end{matrix}O_4\right)_3 . 24H_2O$.

It will be obvious from the above that a very large modicum of common sense requires to be used in the classification of substances as isomorphous, and that each case requires careful consideration. The broad principles, however, which have been of such value in enabling the decisions to be made between rival atomic weights for any one and the same chemical element, are tolerably clear, and they are generally stated more or less in the following form, to which it will be shown in the next section but one (page 1228) that certain reservations, amendments, and limitations must be applied in order that the truth may be accurately represented. The statement is taken, as a current representative one, from the *Theoretical Chemistry* of Nernst (Macmillan & Co., English translation of 7th German edition):

"1. The term isomorphism primarily denotes **identity of crystal form,** which must be shown by complete coincidence of the properties of symmetry, and approximate coincidence of geometrical constants.

"2. The property of forming **mixed crystals** in any selected proportion, at least within certain limits.

"3. The property of **mutual overgrowth,** *i.e.* a crystal of one substance (as a nucleus) increases in size in a solution of the other substance."

To these three characteristics a fourth has been added by Ostwald,[1] namely, the ability to remove the supersaturation of a solution, and so to act as a nucleus for its crystallisation.

These current ideas concerning isomorphism will be critically considered in the next section but one, their limitations established, and the results of the author's own researches utilised to establish the true meaning which should be attached to the term isomorphism, on the lines which have already been briefly laid down on pages 383 and 384.

Historic Instances of the Use of the Principle of Isomorphism to Chemists.—Besides the fixation by Berzelius of the atomic weights of the long list of elements given on page 1223, which occurred at once, automatically and absolutely without ambiguity, there are three most interesting other cases, which merit further notice as being historically noteworthy and particularly illustrative of the use of the principle, namely, those of gallium, columbium (niobium), and vanadium.

Gallium was discovered by Lecoq de Boisbaudran in the year 1875 in the zincblende of the Pyrenees. Its position as a member of the aluminium group of metals, Group III. and series 5 of the periodic table, with atomic weight 69·9, was only after long discussion eventually decided by the fact that its sulphate combines with ammonium sulphate to form a double sulphate isomorphous with the alums. As the constitution of the latter was known to be $R_2'SO_4 . R_2'''(SO_4)_3 . 24H_2O$ it was clear that gallium sulphate must be $Ga_2(SO_4)_3$, and that gallium is a triadic element capable of replacing aluminium in alum. The R_2''' was found in atomic weight determinations with gallium alum to have the value

[1] *Zeitschr. f. phys. Chem.*, 1897, *22*, 330.

139·8, and the atomic weight was thus 69·9. That this conclusion was correct was subsequently most satisfactorily confirmed by the carrying out of successful vapour density determinations with gallium chloride, and by determinations of the specific heat of pure metallic gallium.

The case of columbium, for long called niobium, is even more interesting. This metal belongs to the vanadium-tantalum Group V., in which it is the 6th-series member, with atomic weight 93·5. It was discovered by Hatchett in the year 1801 in a mineral from Massachusetts, and was named by him columbium. In 1802 Ekeberg discovered tantalum in the yttrium minerals of Sweden. In 1809 Wollaston endeavoured to show that the two new elements were identical. Berzelius, however, a few years later proved the separate identity of tantalum. In 1839 Wöhler found that the Bavarian tantalites certainly contain some peculiar ingredient distinct from tantalum, and Rose shortly afterwards isolated the oxide of a metal in columbite from Bodenmais, and called the metal niobium. In 1846 Rose thought he had found another new element in these minerals, and called the acid derived from it hyponiobic acid. In 1865 Blomstrand showed that the chloride of this latter new element contained oxygen, and in fact was an oxychloride. Simultaneously Marignac proved that the double salts which hyponiobic fluoride forms with metallic fluorides are isomorphous with similar double salts containing stannic fluoride SnF_4, titanium fluoride TiF_4, and tungsten oxyfluoride WO_2F_2. As the sum of the atoms is 5 in each of these compounds, and as hyponiobic fluoride was found on analysis to contain 3 atoms of fluorine, Marignac concluded that SnF and TiF of the fluorides of tin and titanium could be replaced by NbO, that hyponiobic fluoride must be an oxyfluoride possessing the composition $NbOF_3$, and that hyponiobium was really the group NbO. On this assumption he found that 48·1 parts of titanium (its atomic weight) were equivalent to 93·5 of the metal in the oxy-group, which he considered was niobium, the same element as was originally called columbium. To complete the proof he also subsequently discovered that the pentoxides of niobium and tantalum occur together in isomorphous mixture in several minerals, that the two double fluorides of potassium and tantalum and of potassium and niobium, namely, K_2TaF_7 and K_2NbF_7, are readily obtained in similar forms and are isomorphous, and that NbO, SnF, and TiF appear to be crystallographically equivalent in various compounds. From the analyses of some of these latter compounds 119·0, 48·1, and 93·5 were found to be equivalent weights for tin, titanium, and niobium, the last of the three numbers representing the true atomic weight of niobium. Similarly, he concluded from analyses of the double fluorides that the atomic weights of tantalum and niobium were 181 and 93·5. Subsequently, but only after the position had been thus correctly determined by Marignac practically entirely from the principle of isomorphism, full confirmation was obtained by the determination, by Deville and Troost, of the densities of the gaseous chloride and oxychloride of niobium, $NbCl_5$ and $NbOCl_3$. It was also fully substantiated that this niobium was identical with the

columbium of Hatchett. Hence, the metal should undoubtedly be called columbium, the name given to it by its discoverer.

Vanadium presents a somewhat similar very interesting case, which was unravelled with great ability by Roscoe. This element—of atomic weight 51·2, the next after phosphorus in Group V., but number 4 of the even series 4, 6, 10 formed by vanadium, columbium, and tantalum—was discovered in the year 1801 by Del Rio, in a Mexican lead ore, and named by him erythronium, from the property of its salts of becoming red when heated with acids. In 1805 Collet-Descotils pronounced the substance to be no new element but only impure chromium oxide. In 1830, however, Sefström described a new metal which he had extracted from the ore of Taberg, and named it vanadium, from Vanadis, another name for the Scandinavian goddess Freia. Wöhler, however, in the same year showed that Del Rio had been correct, and that the Mexican lead ore was vanadate of lead. Sefström then handed his material over to Berzelius, who in 1831 gave the results of a detailed investigation, including the description of a considerable number of vanadium compounds; he classed the metal with chromium and molybdenum. In 1867, however, Roscoe showed that this was an error, and that the substance considered by Berzelius to be vanadium was either the oxide, V_2O_2, or the nitride, VN, according to the mode of preparation. The brilliant metallic-looking scales which Berzelius obtained by heating the oxytrichloride, which he thought was the trichloride, in ammonia gas were found by Roscoe to be not metal but nitride, metallic vanadium possessing the uncommon property of combining readily with nitrogen directly. It was only by reducing the dichloride in hydrogen gas that pure metallic vanadium could be prepared; for the metal also combines directly with oxygen at a red heat to form V_2O_2. Moreover, instead of belonging to the chromium group, Roscoe showed that vanadium is a member of the nitrogen-phosphorus Group V., and that, for instance, the important mineral vanadinite is isomorphous with apatite $Ca_5(PO_4)_3Cl$, and has a similar composition $Pb_5(VO_4)_3Cl$, the lead replacing the calcium and the vanadium the phosphorus of apatite. Vanadium is, in fact, the preceding, even series-member of Group V. to columbium, and, like the latter, in combination with oxygen forms a group vanadyl VO, which replaces the CbO in the compounds referred to in the consideration of the case of columbium (the formula being given on page 1226 as NbO instead of CbO, as at that time the name niobium was current). Thus the recognition of these cases of isomorphism of vanadium compounds, with those of phosphorus and columbium, led Roscoe to a correct determination of the atomic weight of vanadium, to the isolation of the real element, and to the correct placing of the element in the chemical series. Indeed, it was the obvious isomorphism of vanadinite with apatite that first attracted Roscoe to the subject, and led him to reinvestigate the vanadium compounds.

The important results in pure chemistry thus achieved by use of the crystallographic principle of isomorphism afford ample evidence of the value of the principle, when applied with discretion and a due sense of the possible pitfalls. For even Berzelius made great mistakes, as in

the case of vanadium. When adequate crystallographic data are available, including the all essential correct diagnosis of symmetry, the principle affords one of the most valuable of all the aids known in choosing the correct atomic weight, from among the two or three possible alternatives which purely chemical data alone often furnish. The ground is only really sure when the substances supposed to be isomorphous are not only composed of the same number of atoms, but when also the interchangeable elements belong to the same family group of what we now know, thanks to the great later generalisation of Newlands and Mendeleeff, as the periodic classification of the elements (the tabular presentment of which is given on page 768).

We may now proceed to consider the true limits of the law of isomorphism. Incidentally it will also be shown that the determination of these limits decides simultaneously the question of the constancy, fixity, and uniqueness of the crystal angles of any one and the same substance (not belonging to the cubic system), and of its distinction from every other substance by this characteristic property. For, if the law of Mitscherlich held in the extreme form in which he announced it, that of the absolute identity of form of isomorphous substances, it must be obvious that two and often many more substances could have identically the same form (with identical crystal angles), contrary to the law of Haüy.

The True Meaning and Limitation of Isomorphism.—It has already been shown, in the first five pages (380-384) of Chapter XXIV., what are the exact conditions in two typical series of salts other than cubic, which by common consent are isomorphous in the strictest sense in which the term is now admitted to be applicable, namely, series in which the interchangeable elements are members of the same family of chemical elements, of the same group and kind of series, odd or even, of the periodic classification. These two series were particularly suitable for such a study, as likely to exhibit any angular differences at a maximum; for the alkali group of metals are the most electro-positive and chemically vigorous, as bases, of all the groups of elements, and their atomic weights and atomic numbers differ considerably and very regularly, the former constant by 46 or 47 units each time (between K and Rb, and the latter and Cs), and the latter constant by 18 integers (see footnote on page 1235). Moreover, the symmetry is moderately low in one case (rhombic) and very low (monoclinic) in the other. The two series in question are the rhombic alkali normal sulphates and selenates, $R_2' \begin{matrix} S \\ Se \end{matrix} O_4$, and the monoclinic double sulphates and selenates of the series $R_2'M''\left(\begin{matrix} S \\ Se \end{matrix} O_4\right)_2 . 6H_2O$, in both of which series R′ represents potassium, rubidium, or cæsium, the monovalent alkali metals above referred to, of Group I., and the even series 4, 6, and 8 of that group. As will be dealt with more fully later, the R may also represent either the base ammonium NH_4 or the metal thallium in its thallous capacity. A typical set of crystals of the simple rhombic sulphates is shown in Fig. 862*a*, and a similar set of typical crystals of the analogous selenates (except ammonium selenate, which is dimorphous and ordinarily

crystallises in its second, monoclinic, form) in Fig. 862*b*. Three characteristic salts of the monoclinic double sulphate series with six molecules of water are also shown in Fig. 862*c*, the particular salts chosen being

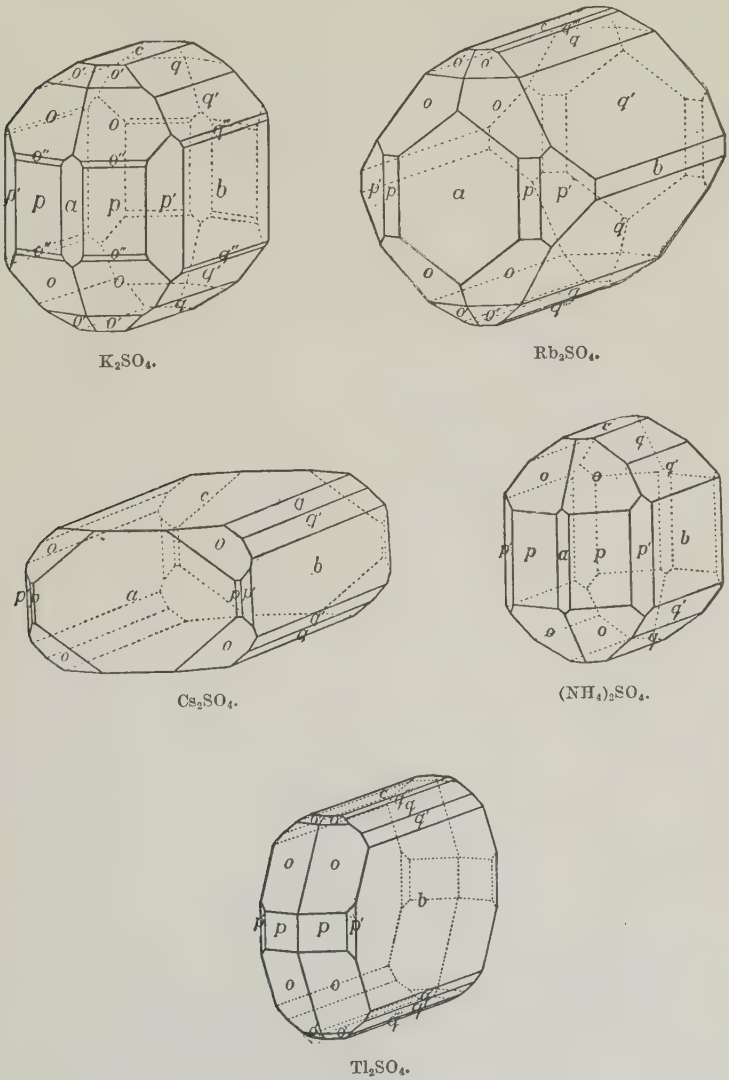
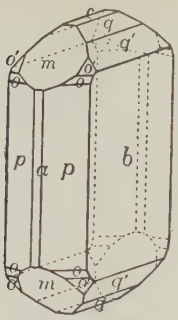
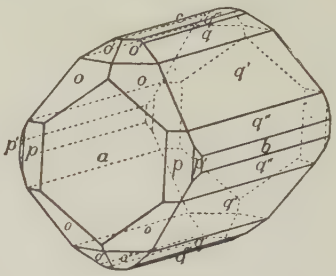


FIG. 862*a*.—The Sulphates of the Alkalies.

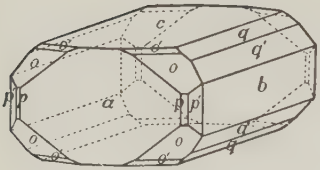
potassium zinc, rubidium zinc, and cæsium zinc sulphates. An analogous set of the three corresponding double selenates is likewise given in Fig. 862*d*.



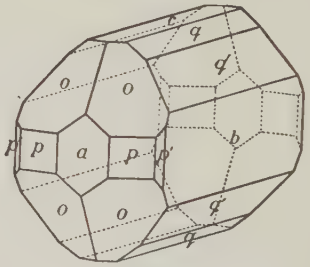
K_2SeO_4.



Rb_2SeO_4.

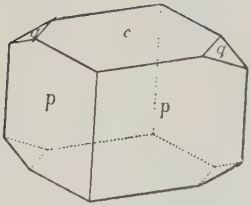


Cs_2SeO_4.

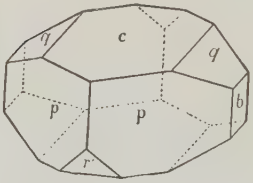


Tl_2SeO_4.

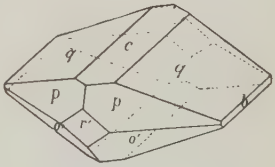
FIG. 862*b*.—The Selenates of the Alkalies



KZn Sulphate.

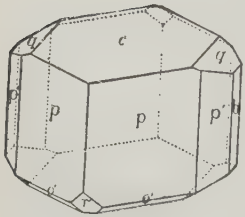


RbZn Sulphate.

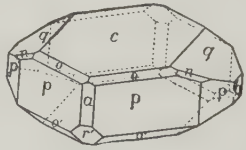


CsZn Sulphate.

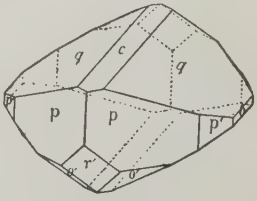
FIG. 862*c*.—Double Sulphates of the Zinc Group.



KZn Selenate.



RbZn Selenate.



CsZn Selenate.

FIG. 862*d*.—Double Selenates of the Zinc Group.

In the rhombic series it was shown that the maximum angular difference was only 56 minutes (in the case of one angle, between potassium and cæsium selenates), or 1° 21′ if the thallium and ammonium salts be included (between potassium and thallium selenates), while in the less symmetric monoclinic series the maximum met with was 2° 28′ (which occurs between potassium copper and cæsium copper selenates in the case of one angle) The angular differences increase as the symmetry diminishes, the maximum for the monoclinic series being more than twice as great as that for the rhombic series. The largest of the average angular differences between any pair of analogous potassium and cæsium salts, that is, the average (mean) value of the differences between the values for analogous angles on these two extreme salts, for all the angles of the two substances compared (the number of quite different angles being 37 in the rhombic series and 36 in the monoclinic series), are 17′ for the rhombic series (between potassium and cæsium selenates), or 28′ if the ammonium and thallium salts be included (between potassium and thallium selenate); and 65′ for the monoclinic series (between KFe and CsFe sulphates), even including the ammonium and thallium salts. In the hexagonal, tetragonal, and trigonal systems the differences are smaller still, and (as will presently be shown for a hexagonal series investigated by Jaeger) approach the possible limits of error of measurement, and except with the most perfect crystals, grown free from any disturbance, are often within the errors of malformation, even of crystals which to all appearance are quite well formed. Eventually, in the cubic system of perfect symmetry, the real differences become zero, while, of course, the casual errors of malformation are still present except in the cases of the most perfect crystals, for which latter the analogous angles are alike to within one minute of arc.

The author has shown, however, that the potassium, rubidium, and cæsium salts of the two series above referred to form an inner circle of isomorphous substances, within which the angular differences are not irregular inside the limits mentioned, but exhibit a regular progression with the atomic weight and atomic number of the alkali metal present; and that this progression is not merely confined to the differences between the external interfacial angles, but extends to the dimensions and volumes of the space-lattice cells, and to the optical and thermal properties. The phenomenon may be diagrammatically illustrated by Fig. 863 (in a very exaggerated manner, as the real change is so small as to be inappreciable on the scale drawn), which represents analogous sections through the crystals of the analogous sulphates or selenates of potassium, rubidium, and cæsium. The inner crystal outline is that of the potassium salt, the outer one that of the corresponding cæsium salt, and the intermediate outline that of the rubidium salt. The vertical lines are the intersections of the two brachypinakoid faces $b = \{010\}$ with a vertical plane parallel to the macropinakoid $a = \{100\}$ in each case; the horizontal lines

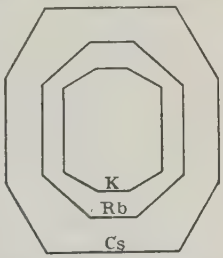


FIG. 863.—Progression of the Crystal Angles of Alkali Sulphates and Selenates.

are the intersections of the two faces of the basal plane $c = \{001\}$ with the same vertical plane; and the oblique lines are the traces of the four domal faces $q = \{011\}$. The diagram shows clearly (purposely exaggerated as stated) the progressive inclination of the last-mentioned domal faces with respect to the brachypinakoid and the basal plane as potassium is replaced by rubidium and the latter in turn by cæsium. Moreover, similar differences occur when the sulphur is replaced by selenium, these two elements also belonging to one and the same Group VI. and odd series 3 and 5 of that group of negative elements.

In these very clear cases of definite chemical relationship the morphological and physical effect of replacing one element by another of the same group and type of series is thus found to be a function of the atomic weight and the atomic number; with regard to some properties it is a direct proportion, but usually it is an accelerating function. Such series, in a review of the author's work [1] by Linck, have been termed "eutropic," from *εὐτροπή*, meaning "a regularly progressive change," a term which is convenient and expressive and which the author has, therefore, adopted. Besides this inner circle of eutropic potassium, rubidium, and cæsium salts, however, the two series investigated by the author include salts of ammonium and thallium (the base-group NH_4 and the metal thallium in its thallous capacity being capable of replacing the alkali metals as the R′ base), which are truly isomorphous but not eutropic, and the exact relationship of which will be dealt with presently. On all these grounds the author, as already foreshadowed on page 384, has been led to the following definition of isomorphism:

An Isomorphous Series is one the members of which bear some definite chemical analogy and crystallise according to the same system of symmetry and in the same class of that system, and develop the same forms, the faces of which are inclined at angles which only differ by a very few degrees, rarely reaching $2\frac{1}{2}°$,[2] the magnitude of the difference being inversely proportional to the degree of symmetry. The most perfect type of isomorphism, to which the term "eutropism" is applied, is displayed when the series is one in which the interchangeable chemical elements all belong to the same family group and type (odd or even) of series of the periodic classification: in such eutropic series the small interfacial angular differences, the dimensions of the space-lattice cells, and the optical and thermal constants, obey the law of progression according to the atomic weight or atomic number of the elements interchanged, the properties of the crystals being thus functions of the atomic number.

A comparative table of the interfacial angles of the rhombic normal sulphates and selenates of the alkalies has already been given on page 382, and a similar table will now be given for a typical group (set containing the same M″-metal) of the series of double sulphates and selenates, that containing zinc as the M″-metal.

[1] G. Linck, *Zeitsch. für phys. Chem.*, 1896, *19*, 197. The derivation given above is quoted from Linck's memoir. Doubtless a better derivation would be from *εὔτροπος*, "readily changing."

[2] The maximum angular difference observed by the author is 2° 28′, between two salts (KCu and CsCu selenates) of the monoclinic series possessing six molecules of water of crystallisation.

Zinc Group of Monoclinic Double Sulphates and Selenates.

Comparison of the Crystal Angles.

Angle.	KZn sulphate.	RbZn sulphate.	CsZn sulphate.	AmZn sulphate.	TlZn sulphate.	KZn selenate.	RbZn selenate.	CsZn selenate.	AmZn selenate.	TlZn selenate.
	° ′	° ′	° ′	° ′	° ′	° ′	° ′	° ′	° ′	° ′
ac =(100) : (001)	75 12	74 7	72 59	73 8	73 44	75 48	74 44	73 49	73 46	74 6
as =(100) : (101)	45 56	45 16	44 28	44 40	45 10	46 19	45 47	45 3	45 1	45 30
sc =(101) : (001)	29 16	28 51	28 31	28 28	28 34	29 29	28 57	28 46	28 45	28 36
cr' =(001) : ($\bar{2}$01)	63 38	64 20	65 15	64 56	64 19	63 12	63 42	64 36	64 36	63 54
cs' =(001) : ($\bar{1}$01)	38 32	38 45	39 9	38 55	38 35	38 22	38 24	38 52	38 52	38 20
$s'r'$ =($\bar{1}$01) : ($\bar{2}$01)	25 6	25 35	26 6	26 1	25 44	24 50	25 18	25 44	25 44	25 34
$r'a$ =($\bar{2}$01) : ($\bar{1}$00)	41 10	41 33	41 46	41 56	41 57	41 0	41 34	41 35	41 38	42 0
ap =(100) : (110)	35 37	35 22	34 51	35 13	35 26	35 52	35 38	35 4	35 26	35 45
pp' =(110) : (120)	19 28	19 28	19 28	19 28	19 28	19 28	19 28	19 28	19 28	19 28
$p'b$ =(120) : (010)	34 55	35 10	35 41	35 19	35 6	34 40	34 54	35 28	35 6	34 47
pb =(110) : (010)	54 23	54 38	55 9	54 47	54 34	54 8	54 22	54 56	54 34	54 15
cq =(001) : (011)	25 58	25 44	25 23	25 33	25 41	26 8	25 50	25 31	25 50	25 47
qb =(011) : (010)	64 2	64 16	64 37	64 27	64 19	63 52	64 10	64 29	64 10	64 13
ao =(100) : (111)	49 10	48 27	47 37	47 52	48 22	49 35	48 59	48 12	48 15	48 43
oq =(111) : (011)	27 34	27 17	27 3	26 57	27 0	27 42	27 19	27 14	27 11	27 0
aq =(100) : (011)	76 44	75 44	74 40	74 49	75 22	77 17	76 18	75 26	75 26	75 43
qo' =(011) : ($\bar{1}$11)	34 42	34 55	35 21	35 5	34 51	34 31	34 37	35 6	35 0	34 32
$o'a$ =($\bar{1}$11) : ($\bar{1}$00)	68 34	69 21	69 59	70 6	69 47	68 12	69 5	69 28	69 34	69 45
co =(001) : (111)	34 54	34 24	33 54	33 57	34 9	35 11	34 34	34 13	34 20	34 15
op =(111) : (110)	43 7	42 42	42 12	42 20	42 39	43 21	43 5	42 36	42 30	42 54
cp =(001) : (110)	78 1	77 6	76 6	76 17	76 48	78 32	77 39	76 49	76 50	77 9
po' =(110) : (11$\bar{1}$)	57 14	57 59	58 42	58 38	58 19	56 50	57 43	58 14	58 4	58 12
$o'c$ =(11$\bar{1}$) : (00$\bar{1}$)	44 45	44 55	45 12	45 5	44 53	44 38	44 38	44 57	45 6	44 39
bo =(010) : (111)	70 5	70 24	70 51	70 39	70 27	69 51	70 13	70 37	70 23	70 17
os =(111) : (101)	19 55	19 36	19 9	19 21	19 33	20 9	19 47	19 23	19 37	19 43
bo' =(010) : ($\bar{1}$11)	65 13	65 13	65 19	65 9	65 8	65 10	65 14	65 22	65 3	65 6
$o's'$ =($\bar{1}$11) : ($\bar{1}$01)	24 47	24 47	24 41	24 51	24 52	24 50	24 46	24 38	24 57	24 54
sq =(101) : (011)	38 21	37 54	37 27	37 31	37 40	38 36	38 2	37 43	37 54	37 46
qp =(011) : ($\bar{1}$10)	86 5	87 7	88 24	88 0	87 24	85 26	86 30	87 37	87 16	86 54
ps =($\bar{1}$10) : ($\bar{1}$0$\bar{1}$)	55 34	54 59	54 9	54 29	54 56	55 58	55 28	54 40	54 50	55 20
$s'q$ =($\bar{1}$01) : (011)	45 19	45 22	45 31	45 25	45 13	45 15	45 8	45 21	45 31	45 4
qp =(011) : (110)	63 47	63 6	62 29	62 27	62 48	64 7	63 30	63 5	62 46	62 58
ps' =(110) : (10$\bar{1}$)	70 54	71 32	72 0	72 8	71 59	70 38	71 22	71 34	71 43	71 58
$r'o'$ =($\bar{2}$01) : ($\bar{1}$11)	34 42	35 1	35 19	35 22	35 11	34 33	34 49	35 2	35 14	35 6
$o'p$ =($\bar{1}$11) : (110)	93 2	92 36	92 25	92 4	92 7	93 10	92 39	92 43	92 17	92 0
pr' =(110) : (20$\bar{1}$)	52 16	52 23	52 16	52 34	52 42	52 17	52 32	52 15	52 29	52 54

A very useful analysis of these tables is next given. It shows the average change and the maximum change of angle which is evoked when the potassium in the potassium salt, the first member of the group, is replaced by each of the other interchangeable bases. That is, the differences for all the 37 (of the rhombic crystals) or 36 (of the monoclinic crystals) angles compared have been tabulated and their averages (mean values) taken, for each replacement, and the largest observed angular difference for each replacement has at the same time been recorded as the maximum change of angle for that interchange.

AVERAGE AND MAXIMUM ANGULAR CHANGES.

I. *Rhombic Series of Alkali Sulphates and Selenates.*

For replacement of	Average Change.	Maximum Change.	For replacement of	Average Change.	Maximum Change.
K in K_2SO_4 by Rb	0° 9′	0° 26′	K in K_2SeO_4 by Rb	0° 11′	0° 36′
,, ,, Cs	0 17	0 50	,, ,, Cs	0 17	0 56
,, ,, NH_4	0 14	0 38	,, ,, NH_4*	not comparable	
,, ,, Tl	0 27	1 16	,, ,, Tl	0 28	1 21

* Ammonium selenate is dimorphous, the common form being monoclinic.

II. *Monoclinic Series of Double Sulphates and Selenates, Zinc Group (as example)*

For replacement of	Average.	Maximum.
K in $K_2Zn(SO_4)_2 . 6H_2O$ by Rb	0° 26′	1° 5′
,, ,, Cs	0 56	2 19
,, ,, NH_4	0 50	2 4
,, ,, Tl	0 35	1 28
K in $K_2Zn(SeO_4)_2 . 6H_2O$ by Rb	0 27	1 4
,, ,, Cs	0 52	2 11
,, ,, NH_4	0 49	2 2
,, ,, Tl	0 41	1 42

The changes for the other groups of the double salts are very similar. The full tables would be too long to quote here in full, but they are given in the original memoirs. A concise tabular summary of the results is, however, given in Table III. The zinc group is also included so that at the foot of the table the mean of the averages, and the mean of the maxima, for similar interchanges throughout the whole series can be given.

Only two of the thallium salts, those of the zinc group TlZn sulphate and TlZn selenate, have yet been obtained in sufficiently perfect crystals for accurate investigation. Also the manganese and cadmium groups are not included in the table, because the potassium salts of these groups have not been obtained at all, although the rubidium salts and especially the cæsium salts of these groups form excellent crystals; there appears to be a critical limit of existence, not improbably about or below the temperature limit of the freezing-point 0° of water, to the life-range of

III. *Summary of Average and Maximum Angular Changes for Monoclinic Double Salts.*

Group.	Average Change for Replacement of K by				Maximum Change for Replacement of K by			
	Rb.	Cs.	NH_4.	Tl.	Rb	Cs.	NH_4.	Tl.
Mg Sulphate	29′	58′	56′		71′	141′	138′	
Zn „	26	56	50	35′	65	139	124	88′
Fe „	32	65	62		72	145	138	
Ni „	27	54	49		63	122	117	
Co „	27	56	52		66	137	127	
Cu „	22	47	39		53	115	101	
Mg Selenate	23	52	53		56	128	129	
Zn „	27	52	49	41	64	131	122	102
Fe „	27	55	54		69	139	139	
Ni „	23	47	45		57	119	110	
Co „	25	53	49		64	136	126	
Cu „	33	61	47		79	148	125	
Mean values	27′	55′	50′	38′	65′	133′	125′	95′

temperature or to the possible structural dimensions of the cells of the space-lattices of these salts, below which these potassium salts probably fall, thus excluding the possibility of their preparation. Another of the potassium salts, potassium iron selenate, is very difficult to prepare, and when obtained rapidly deteriorates and becomes opaque, owing to its temperature limit being not higher than 2° C. At the other extreme, the cæsium salts are remarkably stable and readily prepared, and invariably form clear, transparent crystals which, if desired, can be grown to a considerable size. The temperature limit of possible existence is thus relatively very high, approaching the boiling-point of water in the case of the cæsium salts. There is considerable evidence that the rubidium salts occupy an intermediate position in this respect of temperature limit and stability.

The following striking facts are shown by these tables :

(1) The **average change of interfacial angle** for any group, and also the mean average over all the groups, is just double as much for the replacement of potassium by cæsium as it is for the replacement of potassium by rubidium, corresponding exactly to the doubling of the atomic weight and atomic number.[1]

[1] That this is so will be clear from the following table :

Table showing the Atomic Weights (H = 1) and Atomic Numbers and their Relations.

	K.	Rb–K.	Rb.	Cs–Rb.	Cs.	Cs–K.
Atomic Weights	38·85	46	84·9	47	131·9	$93 = 2 \times 46{\cdot}5$
Atomic Numbers	19	18	37	18	55	$36 = 2 \times 18$

(2) The **maximum change of angle** in any group, and also the maximum observed for the whole series of groups, is for the cæsium replacement of potassium also double that for the rubidium replacement of potassium, the maxima, like the average changes, thus following the law of progression with atomic weight or atomic number of the interchanged metals, the characteristic of eutropic isomorphism.

(3) The **average and maximum changes of angle** for any replacement of potassium by **ammonium** are nearly the same as, usually very slightly less than, when cæsium is introduced for potassium. For the replacement of potassium by the very heavy metal **thallium** (atomic weight 204) the changes are intermediate between those for the cæsium and rubidium replacements of potassium. Thus the law of progression does not apply to the cases of the ammonium and thallium salts, which are not members of the inner eutropic series, but the angular changes brought about by the replacement of potassium by these two bases are within the limits observed in the eutropic series, so that the ammonium and thallium salts are undoubtedly truly isomorphous although not eutropic with the alkali metallic salts.

The non-eutropic isomorphism of the ammonium salts is also shown by slight differences in the cleavage, as compared with the three alkali metallic salts. For instance, in the simple rhombic sulphates one (that parallel $b\{010\}$) of the two cleavages (parallel $b\{010\}$ and $c\{001\}$) common to the alkali metallic salts is suppressed in ammonium sulphate. And in the double salt monoclinic series, besides the excellent cleavage parallel $r'\{201\}$ which is common throughout the whole series, five of the ammonium salts show an additional cleavage parallel to the symmetry plane $b\{010\}$. The difference between the single atom of an alkali metal and the radicle group NH_4 is doubtless making itself felt in these facts.

Conclusions (1), (2), and (3) above are equally true both of the simple rhombic salts and the monoclinic double salts. They are more clearly shown by the latter as the differences are so much larger. As regards the monoclinic series it should be stated that the **change** in the most important angle of all, **the axial angle** β, between the ortho- and basal pinakoids (100) and (001), is directly proportional to the change in atomic weight or atomic number of the alkali metallic elements interchanged. The change is just over one degree for the replacement of potassium by rubidium, and exactly double this, just over two degrees, for the replacement of potassium by cæsium. Thus in the cobalt sulphate group the two changes are respectively 1° 6′ and 2° 13′; and in the iron selenate group they are 1° 7′ and 2° 12′.

It is probable that these crystal-angular differences shown by potassium, rubidium, and cæsium salts of the monoclinic series are the largest that are ever likely to be met with in eutropic series. For the system is next to the lowest in symmetry, and the three R′ metals which by their interchange form the series are, as already stated, the most electro-positive of all the elements, cæsium exhibiting this property at its maximum; they are likely, therefore, to exert the most powerful influence on the crystalline characters, and indeed their predominating influence in this respect is markedly shown in comparison with the very small effect

produced by the interchange of the M''-metals. Moreover, potassium, rubidium, and cæsium are at the maxima of the curve of atomic diameter, Fig. 584*a* on page 712; whereas the M''-metals are near the minima.

This general law of progression within the eutropic series, and formal proof of isomorphism, but not eutropism, within the eutropic limits in the cases of the non-eutropic members of the series, applies not only to the external morphological[1] angles, but also to the topic axial ratios (the dimensions of the space-lattice cells, the spatial expression of the molecular volume in the proportions of the crystal-axial ratios), to the optical property of refractive index and its molecular expression in molecular refraction, to many other details of the optical properties such as amount of double refraction, and to the thermal expansion in all the cases which have been thermally investigated.

The molecular volumes and topic axial ratios of the rhombic alkali sulphates and selenates have already been given on page 641, on the assumption of a pseudo-hexagonal structure, and they will also be found on page 703 of Chapter XXXIII. calculated for a rectangular rhombic space-lattice. The values for these constants for one of the groups of the monoclinic double salt series are given in the next table, the nickel group chosen being quite an average example.

Molecular Volumes and Topic Axial Ratios of Ni Group.

	Molecular Volume.	Topic axial ratios. χ. : ψ. : ω.
KNi sulphate	193·99	6·0170 : 8·1542 : 4·0934
Rb „	203·43	6·1065 : 8·3081 : 4·1723
Cs „	215·90	6·2097 : 8·5416 : 4·2572
NH_4 „	203·91	6·1426 : 8·3312 : 4·1656
KNi selenate	206·14	6·1677 : 8·2598 : 4·1786
Rb „	216·96	6·2533 : 8·4561 : 4·2542
Cs „	229·17	6·3317 : 8·6878 : 4·3378
NH_4 „	216·53	6·2520 : 8·4543 : 4·2678

Both from the simple rhombic series of salts and from the monoclinic double salts the following identical conclusions are to be drawn :—

(1) The **molecular volume** and **topic axial ratios** for the rubidium salt of any group are intermediate in value between the corresponding constants of the potassium and cæsium salts of that group, thus showing a progression with atomic weight and atomic number.

(2) The values of the **molecular volume** and **topic axial ratios** for analogous **ammonium and rubidium salts** are almost identical, indicating that the space-lattice cells of the two salts are of almost equal volume and identical dimensions in space (length of sides).

These conclusions will be shown in Chapter XXXIII. on the X-ray

[1] The strict sense of the word morphology is to be here understood, as derived from *μορφή*, "form," and *λόγος*, "word or discourse"; that is, the science of form, and, in this case, as applied to crystals.

analysis of crystals to be fully confirmed by the results of X-ray spectrometric measurements of the rhombic sulphates, the absolute volumes and edge dimensions of the cells of ammonium and rubidium sulphates being found to be practically identical, precisely as indicated by the molecular volumes and topic axial ratios. The bearing of this conclusion (2) on the valency volume theory of Barlow and Pope has already been referred to on page 736, and will be found discussed more fully in Chapter XXXIII. It will suffice to say here that it conclusively negatives that theory. For the volume of the unit cell of $(NH_4)_2SO_4$ should be at least double that of Rb_2SO_4 if that theory were correct, as the sums of the fundamental valencies present in the two salts are respectively 24 (made up of 2×3 for N $+8\times1$ for H $+2$ for S $+4\times2$ for O) and 12 (made up of 2×1 for Rb $+2$ for S $+4\times2$ for O), even considering nitrogen as only triadic.

As two representative optical properties we may consider (1) the most important specific property, the mean refractive index (mean of α, β, γ for sodium light) of the crystals of the rhombic simple salts, and of a typical group of the monoclinic double salts, and (2) a molecular optical property, the very important molecular refraction. These are presented in the following three tables:

MEAN REFRACTIVE INDICES.

$1/3(\alpha+\beta+\gamma)_{Na.}$

K_2SO_4 . .	1·4952	K_2SeO_4 . .	1·5396
Rb_2SO_4 . .	1·5136	Rb_2SeO_4 . .	1·5545
Cs_2SO_4 . .	1·5635	Cs_2SeO_4 . .	1·5997
$(NH_4)_2SO_4$.	1·5256	$(NH_4)_2SeO_4$.	1·5694
Tl_2SO_4 . .	1·8708	Tl_2SeO_4 . .	1·9575
KZn sulphate	1·4859	KZn selenate	1·5212
RbZn „	1·4897	Rb Zn „	1·5238
CsZn „	1·5054	CsZn „	1·5367
NH_4Zn „	1·4937	NH_4Zn „	1·5308
TlZn „	1·6064	..	..

MOLECULAR REFRACTION, $\frac{n-1}{d}$ M, FOR RAY C.

	Axis *a*.	Axis *b*.	Axis *c*.	Mean, $1/3(\alpha+\beta+\gamma)$.
K_2SO_4 . .	32·01	31·94	32·18	32·04
Rb_2SO_4 . .	37·61	37·52	37·53	37·55
Cs_2SO_4 . .	47·71	47·56	47·17	47·48
$(NH_4)_2SO_4$.	39·29	38·56	38·40	38·75
Tl_2SO_4 . .	64·74	63·47	62·95	63·72
K_2SeO_4 . .	38·46	38·19	38·86	38·50
Rb_2SeO_4. . .	44·00	43·82	44·36	44·06
Cs_2SeO_4 . .	54·41	54·28	54·37	54·35
$(NH_4)_2SeO_4$.	..	45·22	..	45·92
Tl_2SeO_4 . .	75·63	74·47	75·23	75·11

MOLECULAR REFRACTION, $\frac{n-1}{d}$ M, FOR RAY C.

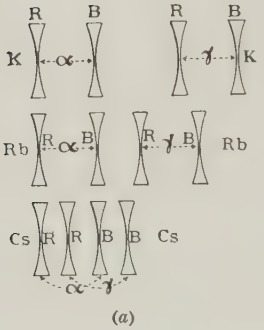
	α.	β.	γ.	Mean, 1/3 ($\alpha+\beta+\gamma$).
KZn sulphate .	93·21	94·33	96·94	94·83
RbZn „ .	98·91	99·91	101·78	100·20
CsZn „ .	108·94	109·51	110·47	109·64
NH_4Zn „ .	100·34	101·21	102·51	101·35
TlZn „ .	121·53	124·82	126·33	124·23
KZn selenate .	106·32	107·55	110·71	108·19
RbZn „ .	112·10	113·39	115·70	113·73
CsZn „ .	122·19	123·02	124·15	123·12
NH_4Zn „ .	113·35	114·63	116·46	114·81

These tables are very briefly summarised in the statement that:

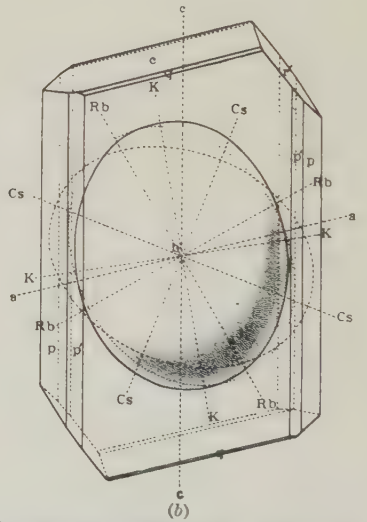
The **refractive index** and **molecular refraction** of any rubidium salt of either series are intermediate between the corresponding values for the analogous potassium and cæsium salts, and nearer to the former than to the latter, in accordance with an accelerating progression according to the atomic weight or atomic number of the interchangeable elements. The values for the ammonium salt are always slightly higher than, but usually very close to, those for the analogous rubidium salt. The optical properties of the thallium salts stand out high above those for the rest of the salts of either series, the thallium salts being thus distinguished by transcendent refractive power, doubtless due to the much higher atomic number of thallium (81), which means greater mass (larger nucleus) and complexity (more cycles or shells of electrons) of its atoms, which thus offer much greater resistance to light vibrations.

As regards the optical properties, the salts of the three strictly comparable alkali metals, potassium, rubidium, and cæsium, thus exhibit the same law of progression as obtains with regard to the morphological properties, and the progression extends to every detail, even the minutest, of these optical properties. Two examples of this wonderful detail in the progression are worthy of special mention, and are illustrated at (*a*) and (*b*) in Fig. 864. The first example concerns the double refraction of any group of either the simple rhombic salts or the monoclinic double salts. The drawing at (*a*) in Fig. 864 represents graphically the regular diminution of double refraction (the difference between the two extreme indices of refraction α and γ) which accompanies increase of the atomic weight and atomic number of the alkali metal present. It exhibits the closing up of the two spectra afforded in succession by each of three analogously orientated 60°-prisms, one ground out of each of the three (K, Rb, and Cs) salts for use in determining two (in this case α and γ) of the three refractive indices α, β, and γ of that salt. Each prism was ground accurately with the correct orientation to afford two spectra, corresponding to the two desired refractive indices, and consequently two images of the signal-slit of the collimator were produced when monochromatic light was being used, as when actually determining the refractive indices. The figure

shows the relative positions of the four images of the Websky slit in red C-hydrogen light (marked R) and in greenish-blue F-hydrogen light (marked B), a pair (R and B) from each spectrum, which serve to locate the ends of the two spectra corresponding to the two indices of refraction in question. It will be observed that the two top spectra, those of the potassium salt, are well apart; those in the second row, of the rubidium salt, are closer together, indicating a reduction in double refraction; while the two lowest spectra, those of the cæsium salt, are so close together that they actually overlap, indicating a still further reduction, the progress of the change being very clearly marked and obviously following the order of the atomic weights and atomic numbers of potassium, rubidium, and cæsium.



Relative Positions of the Two Spectra afforded by 60°-Prisms of K, Rb, and Cs Salts, indicating Progressive Change of Double Refraction.



Progressive Rotation of Optical Ellipsoid on passing from a K Salt to a Rb Salt and thence to a Cs Salt, in Monoclinic Double Sulphates and Selenates.

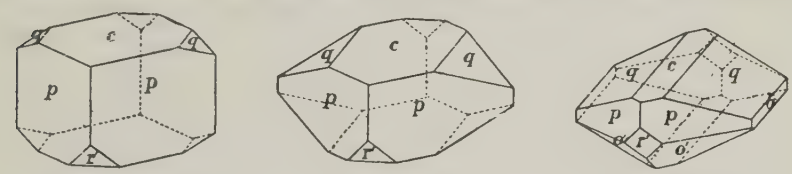
FIG. 864.—Two Examples of Progression of the Optical Properties.

The second example (illustrated at (*b*) in Fig. 864) of the law of progression with atomic weight and sequence number is taken from the investigation of the monoclinic double salts, and refers to the rotation which occurs, with increase of the atomic weight and number of the alkali metal, of the optical ellipsoid about the single axis of symmetry, the axis β of the indicatrix and b of the crystal. In the potassium salt the ellipsoid occupies the position indicated by the ellipse drawn in continuous line in the figure, the section of the ellipsoid by the symmetry plane $b = \{010\}$. The outline of the tabular crystal itself, parallel to the symmetry plane, is also given, as well as the axes a and c of the crystal and those of the ellipsoid lying in that plane. In the rubidium salt the ellipsoid, now represented by the dotted ellipse, has rotated somewhat over to the left, the number of degrees varying slightly for the different

groups (containing the same second metal) of the series of double salts. In the cæsium salt, indicated by the ellipse drawn in broken line, the ellipsoid has swung over considerably more, by a number of degrees which is always greater than for the former rotation, the optical change as regards position of the ellipsoid being an accelerating one with atomic weight or sequence number.

Another of the crystallographic properties, the "habit" of the crystals—that is, their common type of development—also shows a progression, with the atomic number and weight of the alkali metal, in a very striking manner in the case of the monoclinic double sulphates and selenates crystallising with six molecules of water. It is illustrated in Fig. 865, which represents typical potassium, rubidium, and cæsium salts of the magnesium group of double selenates.

The progression is best shown in the relative development of the basal pinakoid $c\{001\}$ and clino-domal prism $q\{011\}$, the former largely predominating in the potassium salt and the latter invariably doing so in the cæsium salt, while in the rubidium salt the two forms are more or less equally developed, the habit of this salt being very clearly of intermediate character. In the cases of the potassium and cæsium salts the



KMg Selenate. RbMg Selenate. CsMg Selenate.

FIG. 865.—The Progression in Habit.

difference is so emphatic that practically no crystal of the one is ever found exhibiting the characteristic habit of the other. When the habit of the potassium salt is prismatic, as it usually is, the prism is parallel to the vertical axis c; the cæsium salt is almost always prismatic, but the prism is parallel to the back-to-front inclined axis a. The rubidium salt of the group is generally of the type shown in the figure, intermediate in every sense between the two very different types displayed so characteristically by the potassium and cæsium salts. Figs. 862*c* and 862*d*, representing typical crystals of the zinc groups, further illustrate these facts.

The author has also determined the **thermal expansion** of the sulphates of potassium, rubidium, and cæsium along the three directions of the rectangular crystallographic axes a, b, c, and from these linear expansions the cubical expansion of each of the three sulphates has been calculated.

The results were as under (for details see pages 1323-1329):

CUBICAL COEFFICIENT OF THERMAL EXPANSION OF ALKALI SULPHATES, $\alpha = a + 2bt$.

For K_2SO_4	$10^{-8}(10475 + 13{\cdot}96t)$
„ Rb_2SO_4	$10^{-8}(10314 + 15{\cdot}34t)$
„ Cs_2SO_4	$10^{-8}(10170 + 16{\cdot}20t)$

Each of the two constants of the formula expressing the cubical expansion is thus seen to show clearly the progression according to atomic weight or atomic number.

These researches of the author are specially collected together and reviewed in the monograph on *Crystalline Structure and Chemical Constitution* (Macmillan & Co., 1910). The additional researches on further groups of the monoclinic series, since described to the Royal Society,[1] confirm still more completely the conclusions arrived at in the monograph. The chief of these final conclusions are quoted and revised up to date below, under the headings (1) to (6).

(1) The crystals of the potassium, rubidium, and cæsium salts of the rhombic series of isomorphous sulphates and selenates of the alkalies, $R_2{}^{S}_{Se}O_4$, and those also of the monoclinic series of double sulphates and selenates, $R_2M\left(^{S}_{Se}O_4\right)_2 . 6H_2O$, whilst conforming to the same symmetry—that of their particular isomorphous series—and exhibiting the same facial forms inclined at angles which never differ by more than one or two degrees, exhibit progressive variations within these limits in their exterior geometrical configurations, interfacial angles, and crystallographic elements, in their internal structural properties and constants of which the external form is only the outward symbol, in their optical characters, and in their thermal behaviour; and these variations follow the order of progression of the atomic weights and atomic numbers of the three alkali metals belonging exclusively to the same family group of the periodic classification, potassium, rubidium, and cæsium, which by their interchange give rise to the series. The variations are therefore functions of the atomic weight and atomic number of the alkali metal, and they have been shown to be usually functions which involve higher powers of the atomic weight or atomic number than the first. It has been further shown that: **Similar variations attend the replacement of sulphur by selenium in the acid radicle present in the salts.**

(2) The whole of the morphological and physical properties of the crystals of such a eutropic-isomorphous series are thus functions of the atomic weights and atomic numbers of the interchangeable chemical elements, belonging exclusively to the same family group of the periodic classification, which give rise to the series. Or, in other words:

The difference in the nature and complexity of the atoms of the chemical elements of the same family group which is manifested in their regularly varying atomic weights, and is intimately related to the atomic number,

[1] *Roy. Soc. Proc.*, 1913, *88*, 361; 1917, *93*, 68 and 72; 1918, *94*, 362; 1919, *96*, 156; 1920, *98*, 67; *Phil. Trans. Roy. Soc.*, 1915, *216*, 1; 1917, *217*, 199; 1919, *218*, 395. Up to and including the 1920 *Roy. Soc. Proc.* memoir, and also one in the *Mineralog. Mag.*, 1912, *16*, 169, describing the isomorphous double chromates belonging to the series (see page 1247), the results for 59 monoclinic double salts of the series with $6H_2O$ have been published, besides those for the 10 simple rhombic sulphates and selenates. The six double selenates containing manganese and cadmium are now under investigation, thus making in all 75 salts studied, all of which have afforded excellent crystals eminently suitable for such a detailed examination and measurement.

is also expressed in the similarly regular variation of the characters of the crystals of a eutropic-isomorphous series of salts of which these elements are the interchangeable constituents.

(3) The radicle ammonium, NH_4, is capable of isomorphously replacing the alkali metal in either the rhombic or monoclinic series, and the general position of the ammonium salt of any group in either series, with respect to the large majority of the crystal properties, is quite close to the rubidium salt, just beyond it on the cæsium side. In respect to the crystal angles, their variations from the potassium salts, either on the average or at the maximum, are slightly less than those between the potassium and cæsium salts. The molecular volumes and topic axial ratios, and the absolute as well as these relative dimensions of the unit cells of the space-lattices of the crystals, of the rubidium and ammonium salts are almost identical, and thus adequately congruent for the crystals to grow together in overgrowths and mixed crystals with the greatest ease.

(4) The metal thallium is also capable of isomorphously replacing the alkali metal in either series, and the position of the thallium salt in the series is remarkably close to that of the corresponding ammonium salt in everything except one very striking difference, which at once sets the thallium salts apart from the whole of the other salts of both series, namely, transcendent refractive power, that is, exceptionally great resistance to the vibration of light waves. While differing thus so markedly in their optical properties, the molecular volumes and molecular distance (topic axial) ratios of the thallium salts are almost identical with those of the analogous rubidium salts, the thallium salts thus behaving in regard to the volumes and dimensions of the space-lattice elementary cells very similarly to the ammonium salts.

(5) The thallium and ammonium salts of the two series of rhombic sulphates and selenates, $R_2{}^{S}_{Se}O_4$, and monoclinic double sulphates and selenates, $R_2M\left({}^{S}_{Se}O_4\right)_2 . 6H_2O$, thus exhibit properties fully entitling them to their inclusion in these respective series of isomorphous salts, understanding by the term " isomorphous series," a series the members of which bear a definite chemical analogy, crystallise with like symmetry, and develop forms the interfacial angles of which differ only by an amount which has not yet been observed to exceed $2\frac{1}{2}$ degrees.

The more exclusive " eutropic series " within each of these isomorphous series, that is to say, the series in which the members exhibit the progression of the whole of the crystal properties according to the atomic weight and atomic number of the interchangeable chemical elements, comprises solely the salts of the alkali metals potassium, rubidium, and cæsium, which belong strictly to the same family group of the periodic classification, the thallium and ammonium salts being excluded by their essentially different chemical nature and their somewhat different crystallographic properties which follow therefrom.

(6) Specific chemical substitutions are accompanied by definitely orientated changes in the crystal structure, indicating that particular

chemical atoms occupy definitely localised positions in the chemical molecule, and therefore, as the molecule or small group of molecules (four in the case of the rhombic series) is the structural unit of the space-lattice, in the crystallographic structural unit.

This latter important fact is particularly well illustrated by the observation that the replacement of one alkali metal by another in the rhombic series of normal sulphates and selenates invariably calls forth a predominating crystallographic change along the direction of the vertical axis *c*, whereas the substitution of selenium for sulphur brings about a preponderating equatorial change. This fact, that each atom entering into a crystalline structure produces a definite and constant crystallographic effect, is shown in Chapter XXXIII. on the X-ray analysis of crystals to be fully substantiated, the actual fixed and definite positions of the various atoms being revealed by the reflections of the X-rays from those atoms.

We are now in a position to add a seventh main conclusion as follows :

(7) **As the above laws governing the inter-relations of members of isomorphous series allocate specific angles and crystal elements, space-lattice cells of definite dimensions, and definite optical and thermal properties, to each individual member of an isomorphous series, they finally confirm the generalisation of Haüy, even in the cases of these very similar substances, that " Every distinct crystallisable chemical substance [not of cubic symmetry] is endowed with a specific crystalline form peculiar and proper to itself."**

These seven laws, together with the definition of isomorphism given on page 1232, define in precise terms and explain the true meaning of Mitscherlich's principle of isomorphism. They indicate the exact and limited sense in which it is correct, and to what extent the literal meaning of the word must be qualified ; and they terminate the long-drawn-out controversy between the disciples of Mitscherlich and those of Haüy, which in his later period Mitscherlich himself deprecated. For they show that both are correct in the main, as regards their broad principles, and the exact details over which they were at cross purposes have now been definitely established with practically general consent.

As regards the **literal isomorphism of cubic substances** as an automatic effect of the high symmetry, it should naturally be understood that only cubic substances obviously closely chemically related should be considered as isomorphous in the sense above accepted. For instance, the alums are such a series, $R_2'\begin{matrix}S\\Se\end{matrix}O_4 . M_2'''\left(\begin{matrix}S\\Se\end{matrix}O_4\right)_3 . 24H_2O$. Yet even here one has occasional doubts with regard to certain members, the sodium alum, for example. Sodium salts are not usually strictly comparable with those of potassium, rubidium, and cæsium, the sulphate of sodium, for instance, being altogether different in character to potassium sulphate, crystallising with ten molecules of water, $Na_2SO_4 . 10H_2O$, whereas K_2SO_4 is anhydrous. Indeed, speaking generally, the sodium salts which crystallise in systems other than the cubic are not usually isomorphous with the analogous potassium salts, sodium belonging to an odd series (3) of Group I. of the periodic table, whereas potassium, rubidium, and

cæsium are even-series metals of that group (4, 6, 8). Yet sodium does form a double sulphate with aluminium sulphate and its analogues, which crystallises like the other alums with $24H_2O$, in class 30 of the cubic system.

In any case, it is only as regards the exterior angles of cubic substances that morphological identity occurs. It is shown in Chapter XXXIII. (page 677) on the X-ray analysis of crystals that for the cubic group of the spinels, $R''R_2'''O_4$, Nishikawa has found that the different members, while externally equi-angular like all cubic substances, possess different individual internal structural characters, the positions of the atoms of the interchangeable elements R''' varying slightly, to about the extent indeed that the external angles change in the systems of lower symmetry. Also, of course, the molecular volumes and topic axial ratios (the relative volumes and linear dimensions of the space-lattice cells), and it would appear from X-ray analysis also the absolute values of those cell volumes and dimensions, vary from member to member of the cubic isomorphous series, as do also the optical, thermal, and other physical properties.

In confirmation of the author's experience with the two extensive rhombic and monoclinic series, that the angular differences between members of an isomorphous series diminish as the symmetry rises, the differences for the rhombic series being much smaller than for the monoclinic series, some very interesting results for an extreme case have been obtained by F. M. Jaeger[1] with a hexagonal (class 25, bipyramidal, like apatite) series of salts, the ethyl-sulphates of the rare earths, $R_2'''(SO_4 . C_2H_5)_6 . 18H_2O$, in which R''' is yttrium Yt, cerium Ce, lanthanum La, neodymium Nd, praseodymium Pr, samarium Sa, europium Eu, dysprosium Ds, gadolinium Gd, erbium Er, neoytterbium Yb, or thulium Tm The crystalline forms prove to be so very nearly rigorously identical that the angular differences fell within the limits of Jaeger's experimental error; the axial ratio $c/a = 0{\cdot}5062 \pm 0{\cdot}0012$. Besides the high degree of symmetry, and the very large restraining mass effect of the remainder of the complex molecule, another cause operates to render the angular difference of these salts small. For, contrariwise to what happens with K, Rb, and Cs, the most electro-positive and vigorous of the metallic elements and of widely differing atomic weight and atomic number, the rare earths differ very little, especially in their sub-groups, in atomic weight and atomic number, and are chiefly metals of the more central less active groups of the periodic system; they are, indeed, so notoriously alike in properties that it has only been by prodigious labour and extraordinary methods of fractionnation that they have been separated. Moreover, it has been shown on page 774 that from cerium to the end of the rare earth elements (two whole periods) there are no electrons added to the outer shells of the atoms, the evolution occurring by internal addition of electrons, without increasing the size of the atoms. These four causes have thus combined to produce a series of isomorphous salts almost as completely identical in crystal angles as a cubic series, the angles of the individual members of the series differing by only a very few minutes, in many cases less than 5′.

[1] *Recueil des trav. chim. des Pays-Bas*, 1914, *33*, 343.

That this hexagonal case of rare earth compounds brought forward by Jaeger is exceptional, however, and quite an extreme case, is clear from two well-known cases of trigonal symmetry, the calcite group [1] of minerals and the red silver minerals.

The principal angle, the rhombohedral angle *rr*, of the crystals of the calcite group varies from 72° 20′ to 74° 55′, as will be clear from the following table of the values of this angle, according to Miers (*Mineralogy*, p. 215), for the various members of the group:

VALUES OF RHOMBOHEDRAL ANGLE IN THE CALCITE GROUP.

Calcite, $CaCO_3$	74° 55′
Magnesite, $MgCO_3$	72 36
Chalybite, $FeCO_3$	73 0
Calamine, $ZnCO_3$	72 20
Rhodochrosite, $MnCO_3$	72 58

The red silver ores, proustite, sulpharsenite of silver, Ag_3AsS_3, and pyrargyrite, the analogous sulphantimonite of silver, Ag_3SbS_3, were elaborately investigated by Miers [2] in the year 1887. These two minerals form exceptionally beautiful crystals (very sensitive to light) of trigonal symmetry, the hexagonal prism of the second order (101) being always a prominent form, terminated by a rich display of end-forms, among which the hemimorphic semi-forms of the primary and subsidiary rhombohedra, scalenohedra, and various pyramidal forms occur. A typical crystal has already been illustrated in Fig. 380 on page 477, and a complete gnomonic projection is given in Fig. 381, page 478. The rhombohedral (primary) angle in the case of proustite is 72° 12′, and that of pyrargyrite is 71° 22′. We have here a case of close (eutropic) isomorphism, for the interchangeable elements, arsenic and antimony, are members of the same family (the first member of which is phosphorus), Group V. of the periodic classification, and of the same type of series (odd, Nos. 5 and 7) in that group. The difference for this primary angle is thus less than a degree, namely 50′, but is still considerable and readily measurable. The numerous other angles measured by Miers also show clearly measurable differences. Hence, even in these cases of fairly high symmetry, in the absence of special circumstances such as those surrounding the rare earths, readily measurable differences are found to exist between isomorphous (even eutropically so) substances.

In concluding this section it should also be stated that two orthorhombic series of salts, the permanganates of potassium, rubidium, cæsium and ammonium, and the perchlorates of these same bases and thallium, $R'MnO_4$ and $R'ClO_4$, have been investigated as far as their morphology is concerned by Muthmann [3] and by Barker [4] respectively. The results are exactly in line with those of the author for the sulphates and selenates, and this independent confirmation is very welcome and satisfactory. Further details of these results will be found on page 1253.

[1] For the structure of this group of minerals as revealed by X-rays see page 680.
[2] *Mineralog. Mag.*, 1888, *8*, 37.
[3] *Zeitschr. für Kryst.*, 1894, *22*, 547.
[4] *Journ. Chem. Soc.*, 1906, *89*, 1132.

The author[1] has also carried out, in collaboration with Miss M. W. Porter, an investigation of a group (the magnesium group) of the monoclinic double chromates $R_2'M''(CrO_4)_2 . 6H_2O$, the results being remarkably in line with those for the double sulphates and selenates, showing that the three series formed by sulphur, selenium, and chromium (in its chromic acid form) are truly portions of the same great isomorphous series. But the chromium series is not eutropic with the other two series in which sulphur and selenium are interchangeable, which two latter series probably are eutropic. The ammonium magnesium and rubidium magnesium chromates are practically isostructural, like the other Am and Rb pairs of salts. The potassium salt $K_2Mg(CrO_4)_2 . {}_6H_2O$ was not obtained, doubtless for a reason similar to that already mentioned, which prevents the formation of the potassium salts of the manganese and cadmium groups of double sulphates and selenates. In the year 1919, however, it was fugitively obtained by A. Duffour,[2] but proved to be exceedingly unstable; for if the temperature exceeded 10° C. the crystals became opaque within 5 hours, and became converted into a mass of minute crystals of the triclinic dihydrate. Duffour was just able to make a few measurements of the crystals at low temperatures before their decomposition, and the angles proved to be related to those of the rubidium and cæsium salts precisely as in the cases of the double sulphates and selenates, the rubidium salt being intermediate as regards the values of its crystal angles. For instance, the important axial angle *ac*, β, of Duffour's potassium magnesium chromate was 103° 54′, the corresponding angle of the rubidium salt having been found by us to be 104° 49′, and that of cæsium magnesium chromate to be 106° 4′.

Mixed Crystals, Overgrowths and Parallel Growths, and their Relation to Isomorphism.—These three very much discussed subjects are intimately connected with each other and with the subject of isomorphism, and a clear explanation has only been afforded by the development of the recent work on molecular volumes, topic axial ratios, and the X-ray analysis of crystals. As the combined result of these investigations it may be said at once that:

The formation of parallel growths, overgrowths and mixed crystals, is dependent on close similarity in shape and size of the elementary (unit) cells of the space-lattices which form the foundation of the crystal structure. The space-lattice must not only be of the same type of symmetry, as is the case for all the members of isomorphous series of substances, but also the relative and absolute dimensions of the unit cells must be very nearly identical; the nearer to identity the more perfect the overgrowth or admixture, the outer limit of approach towards identity corresponding to the formation of parallel growths, while the closer and still closer approximation corresponds to overgrowths, zonal growths, or complete admixture. This means closeness to equality both in the molecular volumes and topic axial ratios, and in the absolute cell volumes and cell side or edge dimensions as determined by the X-ray spectrometric method.

Thus, for instance, the rhombic series of sulphates of potassium,

[1] *Mineralog. Mag.*, 1912, *16*, 169. [2] *Comptes Rendus*, 1919, *169*, 73.

rubidium, cæsium, and ammonium have been shown to have the values of all these constants which will be found on page 703 of Chapter XXXIII. It will be observed that, in accordance with the progression according to atomic weight and atomic number, there is a considerable difference as regards all these constants between the two extreme members of the series, potassium and cæsium sulphates, but naturally much less difference between either of these extreme members and the intermediate member rubidium sulphate, and that the values for the latter are nearly identical with those for ammonium sulphate. Similar relationships hold as regards the selenates. Now it is a fact, in full agreement with the above statement, that parallel growths, overgrowths, and mixed crystals cannot be obtained of potassium and cæsium sulphates or of the selenates of the same two metals; they can be obtained, with some patience and possibly some turbidity, of the analogous potassium and rubidium or cæsium and rubidium salts. But the rubidium and ammonium salts form mixed crystals, overgrowths, zonal growths, and parallel growths (which almost immediately become complete overgrowths) with the greatest facility, by virtue of their almost identical structural-cell dimensions. The beautiful work of Barker on parallel growths and overgrowths has already been discussed at some length on page 498, and it is fully confirmed by the researches of other workers, notably those of Wulff already referred to. The author's own remarkable experience in the case of ammonium selenate has also been referred to on page 514, and again in more detail on pages 738 and 739. Moreover, it will be found described in Chapter XXXIII. how that Prof. Ogg and Mr. F. Lloyd Hopwood, working in Prof. Bragg's laboratory and employing the identical crystals of the salts prepared with great care by the author, have been able to determine the absolute dimensions of the cells of the space-lattices of these rhombic sulphates, and have found these actual measurements to be related precisely as are the topic axial ratios given by the author, the absolute values for the ammonium and rubidium salts being almost identical.

There has been very much discussion and controversy as to the nature of **mixed crystals.** The question has been: "When two substances crystallise together, do they form distinct alternating layers, as has been suggested by Retgers in voluminous memoirs, or do the molecules of the two substances mingle as if there were but one substance present? And if the latter occur, will the structural constants be a mean between those of the constituents (assuming the usual slight variation between the dimensions of the different members of an isomorphous series), taking into account the proportions of the two ingredients present?" A decided answer would now appear to have been given to these questions, as another advance due to the new use for X-rays in probing crystal structure. An investigation attended by definite results has been carried out by Vegard and Schjelderup,[1] employing the Bragg X-ray spectrometric method described in Chapter XXXIII. They commence their memoir with an excellent review of the very considerable literature on the subject. They

[1] *Phys. Zeitschr.*, 1917, *18*, 93.

point out, as already indicated by Barker[1] in the year 1908, that there are two schools of thought, corresponding to the two alternatives presented in the questions propounded above. The one is represented by the views of Retgers, who from numerous experiments, which from their very nature could never be conclusive, suggested that the phenomenon is purely mechanical, mixed crystals being formed of series of thin homogeneous laminæ. The other is represented (according to the statement of Vegard and Schjelderup) by the views of Wulff,[2] Gossner,[3] and Tutton,[4] who consider that the mixing is of a more intimate nature, one or two atoms of one constituent being replaced, here and there, at some of the nodes of the same space-lattice, by a corresponding atom or atoms of the other; these three investigators have shown that the magnitude of the molecular volume plays a decided part in the formation of mixed crystals, in that the molecular volumes of both substances must not be widely different, this being a necessary condition for miscibility. It is the latter fact that has led these three workers to the view that an intimate union occurs between the two components, and one of them, Gossner, has stated still further important grounds for this assumption.

Before proceeding to describe the results of Vegard and Schjelderup, a word or two of detail, as to the experiments of Wulff, Gossner, and the author, are necessary in order to make their position clear. Wulff observed that ammonium sulphate (mol. vol. 74·04) mixes completely to give perfect mixed crystals with rubidium sulphate (mol. vol. 73·34), and also, but not so perfectly or in such good crystals, with either potassium sulphate (mol. vol. 64·91) or cæsium sulphate (mol. vol. 84·58); potassium and cæsium sulphates, however, he found totally immiscible, and he ascribed this to their inability to fit together, owing to great difference of molecular volume.

Gossner observed that the isomorphous hexagonal salts $ZnSiF_6 . 6H_2O$ (mol. vol. 145·6) and $NiSiF_6 . 6H_2O$ (mol. vol. 144·6) mix in all proportions, while the former is quite immiscible with the isomorphous salt $ZnSnF_6 . 6H_2O$ (mol. vol. 166·0), and he attributed the reason to the considerable difference of molecular volume.

The author (Tutton) had already arrived quite independently at the facts stated by Wulff, as the result of careful redeterminations of the density of the crystals of the alkali sulphates by the new Retgers method of floating in a mixture of methylene iodide and benzene of exactly the same density; and the author also added other facts from the study of the selenate group, notably that rubidium and ammonium selenates (mol. vols. 79·94 and 81·12) crystallise together in large and very perfect transparent rhombic mixed crystals, which may contain more than 60 per cent. of the ammonium salt, although the latter salt in the pure state can never be obtained at all in rhombic crystals, the common form stable at the ordinary temperature being the monoclinic, the salt being dimorphous. Indeed, it is probable that if the rhombic form of ammonium

[1] *Mineralog. Mag.*, 1908, *15*, 48.
[2] *Zeitschr. für Kryst.*, 1906, *42*, 558. [3] *Zeitschr. für Kryst.*, 1907, *43*, 130.
[4] *Journ. Chem. Soc.*, 1906, *89*, 1059; and *Proc. Roy. Soc.*, A, 1907, *79*, 373.

selenate could be prepared in good crystals their density would be slightly greater than that of the monoclinic form, which had necessarily to be used in calculating the molecular volume; the molecular volume for the rhombic form would thus be still closer to that of rubidium selenate than is shown by the numbers just quoted.

It should also be mentioned that Barker has proved (*loc. cit.*) that the necessary degree of closeness of molecular volume and of topic axial ratios is much greater for miscibility than for the mere formation of parallel growths. Moreover, the conditions are quite different; for when one salt grows in parallel position over another (as in the case of sodium nitrate $NaNO_3$ over calcite $CaCO_3$, illustrated in Fig. 396 on page 499) the values of the angles of the crystals deposited do not tend to approximate to those of the mother crystal; for the latter is already a fixed solid and cannot reciprocate by meeting the depositing substance half-way and to that slight extent altering its own angles. But when mixed crystals are formed the substances can accommodate themselves to each other, the result being a structure with intermediate angles. The accommodation occurs in all probability both just before and during solidification. In the case of deposition on an isomorphous ready-formed crystal, when the molecular volume and topic axial ratios of the depositing crystalline substance are very close to those of the solid already present as a crystal, the growth usually takes the form of a zonal growth or complete overgrowth, and no longer as isolated small crystals arranged parallelwise with the structure of the parent crystal.

To return now to the investigation of Vegard and Schjelderup, they have proved that the X-ray spectrometric method of crystal structure analysis affords the means of deciding this important question as to the intimate nature of mixed crystals. For, if mixed crystals be composed of two sets of thin homogeneous alternating laminæ, each component must produce its own X-ray spectrum, and the spectrum of the mixed crystal should be a superposition of the two separate component spectra. If, however, the mixed crystal behave as an entity, the atoms of both substances taking their places in a combined configuration, a single and different X-ray spectrum would result. Vegard and Schjelderup have carried out a whole series of experiments to ascertain the facts, using the Bragg X-ray spectrometer. Four cases of mixed crystals were tested, three being mixtures of potassium chloride and bromide, KCl and KBr, in different molecular proportions, and one being a mixture of potassium and ammonium bromides, KBr and NH_4Br. The reflections from the cube, rhombic dodecahedron, and octahedron faces were all investigated. The result was that **the crystals were found to reflect X-rays as entities,** the spectra being normal. That is, they were not composed of two superimposed spectra with double reflection maxima, but consisted in each case of a single maximum of reflection, at a glancing angle which was intermediate between the angles which were observed with crystals of the two constituent pure substances. The authors, therefore, consider the test decisively against the Retgers view of thin alternating laminæ, and in favour of the views of Wulff, Gossner, and the author. This

result is striking, and deeply interesting as being another brilliant outcome of the use of X-rays as revealers of crystal architecture.

It would thus appear, as Gossner and the author have concluded from much definite experimental evidence, that in the mixed crystal a new configuration arises, with a corresponding minute change in the volume and linear dimensions of the space-lattice unit cell, and the molecular volume must be considered as also correspondingly modified. The adjustment occurs through the atomic forces, which doubtless together make up the force of crystallisation. The new atomic arrangement, corresponding to the observed maxima of reflection, is worked out by Vegard and Schjelderup for each of the four cases studied. It must be remembered that all the configurations, those of the two components when in separate crystals of the pure substances and the intermediate new configuration of the mixed crystal, are all very nearly identical, and are absolutely so in symmetry. The view of Wulff, Gossner, and the author, that mixed crystals are true homogeneous structures, and that only those members of isomorphous series form them which are fairly close together in molecular volume, is explained on the assumption that the force of crystallisation brings about actual equalisation of the molecular volumes, one constituent contracting to a minute extent and the other expanding to the same extent in the act of crystallising together; the amount of such change of volume is only of the same order as the author has actually found to occur in his determinations of the thermal expansion of the sulphates of the alkalies (see pages 1241 and 1323-1329). This view is now thus confirmed in a most satisfactory manner by the X-ray work of Vegard and Schjelderup. Moreover, further confirmation, if any were needed, has since (1919) been afforded by the results of a research by F. Rinne,[1] who has submitted a considerable number of pure substances and their mixtures to X-ray analysis. The substances comprised the cubic elements aluminium, copper, silver, gold, and lead; the rhombohedral carbonates of magnesium, calcium, manganese, iron, zinc, and cadmium; and the cubic haloid salts of lithium, sodium, potassium, rubidium, and cæsium. The results indicated clearly that in isomorphous mixtures of the members of each of these groups of substances the vicarious constituents replace one another atom for atom or group for group in the crystal lattice. It is thus absolutely certain that closeness of molecular volume and congruency of topic axial ratios, in other words, close approximation to the identity of the volume and dimensions of the space-lattice cells, that is, compatibility of the structural dimensions, are the conditions for the ready formation of mixed crystals, zonal growths and overgrowths, parallel growths being still possible when the dimensions are not quite so close.

Very beautiful cases of overgrowths are those afforded by the immersion of crystals of zinc sulphate (mol. vol. 146·7) in a solution of magnesium sulphate (mol. vol. 147·1), and of chrome alum crystals (mol. vol. 542·2) in a solution of potash alum (mol. vol. 541·6).

Again, the notorious formation of zonal growths of one felspar on

[1] *Centr. Min.*, 1919, 161.

another is due to a similar cause, for the molecular volumes of the extreme members of the group, albite and anorthite, are 100·1 and 101·5, so close, in fact, that the difference is less than 1½ per cent.

It must not be overlooked also that there is frequently very intimate admixture of the interchangeable constituents of an isomorphous series in naturally occurring minerals. For it is rare to find a mineral composed of the absolutely pure salt which it is supposed to be. Analysis generally reveals the presence, either as traces or larger quantities, of other members of the same family of elements, which thus vicariously replace equivalent quantities of the main element. It is this fact which is responsible largely for the difficulty often experienced in determining the composition of a newly discovered mineral. It is also this same fact which renders it usually much more satisfactory to work, in crystallographic investigations, with artificially prepared pure substances, the composition of which is definite, rather than with naturally occurring minerals.

Perhaps the best example of "vicarious" isomorphous replacement is afforded by the garnet series of cubic minerals, $R_3''R_2'''(SiO_4)_3$. The principal members of the garnet group are the following, in which R'' is calcium, magnesium or iron, and R''' is aluminium, iron or chromium:

Grossular	$3CaO . Al_2O_3 . 3SiO_2$
Pyrope	$3MgO . Al_2O_3 . 3SiO_2$
Almandine	$3FeO . Al_2O_3 . 3SiO_2$
Andradite	$3CaO . Fe_2O_3 . 3SiO_2$
Uvarovite	$3CaO . Cr_2O_3 . 3SiO_2$

From the constitutional manner in which these formulæ are expressed, it will be obvious that there are two sets of vicarious constituents, one set consisting of CaO, MgO, and FeO, and the other set comprising Al_2O_3, Fe_2O_3, and Cr_2O_3. Many garnets contain small quantities of the other vicarious possible constituents than the two main ones constituting the particular mineral.

Unusual Types of Isomorphism.—It will have been seen from the foregoing that the original definition of isomorphism given by Mitscherlich, and even his later one, has been narrowed down to denote the similar structures of compounds of the same type, in which the interchangeable elements belong to the same group of the periodic system, the chemical structure and distribution of valencies remaining the same. It has, however, been also shown that there are some cases of undoubted isomorphism which cannot be brought within the limits of such a definition, for instance, the isomorphism of ammonium and thallium sulphates, $(NH_4)_2SO_4$ and Tl_2SO_4, with potassium sulphate K_2SO_4 and its undoubted family analogues rubidium and cæsium sulphates, Rb_2SO_4 and Cs_2SO_4. Ammonium is a radicle group NH_4, while thallium is a metal of dual character. It belongs to Group III. of the periodic system, and when acting with its higher triadic valency is allied to aluminium and the other triadic analogues of Group III., forming the thallic salts such as the sulphate $Tl_2(SO_4)_3$, but in its lower monadic capacity it simulates some of the properties of the alkali metals, forming thallous salts.

In the same way there is the remarkable case of calcite $CaCO_3$ and sodium nitrate $NaNO_3$,[1] both of which crystallise in rhombohedra the angles of which are very close together, namely, 74° 56′ (as measured by the author, see page 378) and 73° 27′; the molecular volumes of the crystallised substances are also nearly identical, 36·8 and 37·8, so that, as Kopp long ago showed and Barker has more recently brought into prominence, sodium nitrate forms excellent parallel growths (see page 499, with Fig. 396) on calcite. That it is a case of isostructure is quite clear, because sodium nitrate absolutely refuses to form parallel growths on the analogous carbonates of iron, zinc, and manganese, $FeCO_3$ (chalybite, mol. vol. 30·2), $ZnCO_3$ (calamine, mol. vol. 28·2), and $MnCO_3$ (rhodochrosite, mol. vol. 31·0), or on dolomite $(CaMg)CO_3$ (mol. vol. 32·1), all of which have molecular volumes and topic axial ratios too considerably removed. The topic axial ratio χ for calcite is 4·0478, and for sodium nitrate 4·1276; the values for chalybite, calamine, and rhodochrosite are 3·8432, 3·7763, and 3·8781. Moreover, the parallel growths of sodium nitrate are not only deposited on the rhombs of Iceland spar, but also on any other of the forms of calcite, on the scalenohedra of dog-tooth spar for instance. Thus the unit-structural cells of sodium nitrate are more compatible and congruent with those of calcite than with any other member of the rhombohedral carbonate group, and parallel deposition occurs in that case only, in consequence of the fulfilment of the requisite condition. The fact that the number of atoms is the same in sodium nitrate and in all the four carbonates, however, and that the structure is similar, renders it more or less illogical not to consider the five substances all isomorphous with one another.

Another case which has been investigated by Barker (*loc. cit.*) is that of rhombic potassium perchlorate and barytes, $KClO_4$ and $BaSO_4$, which crystallise in very similar forms and the former of which deposits excellent parallel-growth crystals on the latter, owing to close congruency of the structural units of the two substances, the molecular volumes and topic axial ratios being very nearly the same. Now each is a member of a rhombic isomorphous series, that of barytes including celestite $SrSO_4$ and anglesite $PbSO_4$ (anhydrite $CaSO_4$ not being isostructural as it has a different cleavage), and that of which potassium perchlorate is a member being a double series which includes both the perchlorates and permanganates of potassium, rubidium, cæsium, ammonium, and thallium. The degree of isomorphism between the perchlorates and permanganates is comparable with that between the sulphates and selenates of these same five bases. The permanganates and perchlorates, as already mentioned, have been investigated as regards their goniometry and volume constants by Muthmann (*loc. cit.*) and by Barker (*loc. cit.*) respectively, and found to be related in a similar manner to that described by the author for the sulphates and selenates; the potassium, rubidium, and cæsium salts exhibit the same progression according to atomic weight or atomic number, the rubidium salt being always intermediate; moreover, the dimensions of the structural-unit cells of the ammonium salt of each

[1] For the structure of both substances as revealed by X-rays see page 683.

group have been found to be remarkably close to those of the rubidium salt of that group. The following table will render this clear, as regards both the progression of the principal angles and that of the volume constants, molecular volume and topic axial ratios. Separately, at the foot of the table, some corresponding constants for the three barytes minerals are also given.

Crystallographic and Volume Constants of Permanganates and Perchlorates and Barytes Group.

	$m:m$.	$c:q$.	$c:r$.	Mol. Vol.	χ.	ψ.	ω.	ξ.
$KClO_4$	76° 1′	52° 1′	39° 19′	54·91	3·7360	4·7878	6·1307	3·0365
$RbClO_4$	77 5	..	38 57	61·33	3·9244	4·9264	6·3447	3·1492
$CsClO_4$	78 31	52 23	38 27	70·05	4·1625	5·0929	6·6086	3·2888
$AmClO_4$	76 50	52 1	38 55	60·19	3·8959	4·9117	6·2909	3·1346
$TlClO_4$	77 10	..	38 57	62·66	3·9964	5·0093	6·2606	3·2040
$KMnO_4$	77 8	52 24	39 9	58·53	3·8555	4·8360	6·2779	3·0924
$RbMnO_4$	79 28	53 7	38 48	63·23	4·0362	4·8565	6·4704	3·1574
$CsMnO_4$	81 56	53 53	38 17	70·04	4·2551	4·9005	6·7161	3·2450
$AmMnO_4$	78 28	52 47	38 53	62·13	3·9757	4·8698	6·4126	3·1433
Barytes	78 23	..	..	52·0	3·6509	4·7899	5·9472	3·0113
Celestite	75 58	..	..	46·8	3·5349	4·5931	5·7649	2·8980
Anglesite	76 17	..	..	48·2	3·5743	4·5520	5·8694	2·8938

Now it will be clear from this table that there is much closer compatibility and congruency between potassium perchlorate and barytes than between any other member of the perchlorate-permanganate group and the barytes group, and it is just between these two that the phenomenon of parallel growths is observed; the next nearest is potassium permanganate, and this salt shows also some tendency, but a lesser one, to form such growths. The rest do not exhibit the phenomenon at all. From the foregoing it is obvious that we find great difficulty in denying the relationship of isomorphism between calcite and sodium nitrate, and between potassium perchlorate and barytes. Moreover, Barker[1] has shown that there is a remarkable isomorphism between the two latter substances and the borofluoride of potassium, KBF_4. A useful list of extraordinary cases of isomorphism is given in this 1912 memoir of Barker (page 2487), in which are included the singular group alluded to on page 1226, in which the oxy-groups CbOF and WO_2 replace the group TiF_2. Two other unusual cases are the replacement of CaSi by 2Al in the pyroxenes, and NaSi by CaAl in the felspars; for albite, $NaAlSi_3O_8 = NaSi(AlSi_2O_8)$, and anorthite, $CaAl_2Si_2O_8 = CaAl(AlSi_2O_8)$.

[1] *Journ. Chem. Soc.*, 1912, *101*, 2484.

CHAPTER LV

POLYMORPHISM, ISOGONISM, AND ENANTIOMORPHISM

Polymorphism.—The occurrence of one and the same substance in more than one crystalline form has already been referred to in the last chapter, and several instances have been quoted, notably those of calcium carbonate (trigonal calcite and rhombic aragonite), sulphur (ordinary form rhombic, second form monoclinic, produced after fusion and partial resolidification), and the sulphates of magnesium, zinc, nickel, iron, and cobalt, $M''SO_4 . 7H_2O$ (rhombic and monoclinic). An exceptionally interesting case, which will be dealt with in detail in Chapter LVII., is that of silver iodide, AgI, which is hexagonal at ordinary temperatures, but changes suddenly to cubic at 146° C. Another remarkable case, that of ammonium selenate, $(NH_4)_2SeO_4$ (monoclinic, but rhombic when mixed with other alkali sulphates or selenates, like these other salts of the series), has already been referred to on page 1248 in the preceding chapter, and given in some detail on pages 514 and 738.

To these dimorphous cases may be added the trimorphous case of titanium dioxide, TiO_2, also already mentioned on page 198, which occurs naturally in the two distinct tetragonal forms of rutile and anatase (the measurement of a crystal of which is described in Chapter XIII.), and the rhombic form of brookite. Ammonium nitrate, NH_4NO_3, according to Lehmann[1] is even tetramorphous, and the limits of stability for all four forms occur between the ordinary temperature and the melting point of the dry salt, 168° C. The fused salt first solidifies in isotropic skeletal crystals. On cooling to 125·6° the mass becomes suddenly doubly refractive, and in the case of a solution at this temperature optically uniaxial crystals are deposited (rhombohedra[2]). On cooling further, at 82·8°, from among the growths of the last-mentioned form rhombic needles appear, having a particular orientation towards the crystals of the rhombohedral form. Finally, at 32·4°, these rhombic crystals change into a fourth modification, also of rhombic symmetry, and it is this form which is obtained in large flat tabular or acicular crystals by the evaporation of aqueous solutions at the ordinary temperature. When these crystals of the ordinary form are warmed they

[1] *Zeitschr. für Kryst.*, 1877, *1*, 106.
[2] According to Wallerant this form is tetragonal.

become converted successively at the proper temperatures into the three other forms. Schwarz has determined the densities, specific volumes, and specific heats of all four varieties. A considerable increase of volume occurs on conversion of the uniaxial form into the cubic, and of the ordinary rhombic form into the other rhombic form; the conversion of the latter rhombic form into the trigonal form is, however, accompanied by contraction. The needle-shaped crystals of the ordinary form exhibit remarkable plasticity, being capable of being bent into a V shape or into a loop, as more fully described on page 555.

A case of dimorphism which may be readily demonstrated under the microscope is that of antimony trioxide, Sb_2O_3, the photomicrograph of a slide of which is reproduced in Fig. 866. The slide was simply obtained by subliming a little of the oxide, heated gently in a test tube, on to a cool microscope-object 3 by 1-inch slip. The vapour condensed in crystals on the slip, and on examination under the microscope both varieties, rhombic and cubic, were found to be present, the former in the shape of long acicular prisms and the latter in isolated octahedra, which were often found perched on the needles, as shown in Fig. 866.

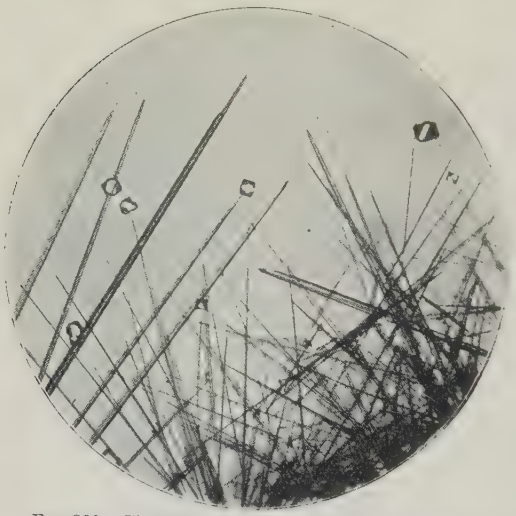


FIG. 866.—The two Crystal Forms of Antimony Oxide.

In the well-known clear cases which have been referred to there can be no doubt that the polymorphism is due to the ability of the molecules of the substances in question to form two or more different space-lattices, within the temperature limits of ordinary observation. That is, at a series of ascending or descending temperatures, assuming the pressure to remain the ordinary atmospheric, these different types of homogeneous structures are produced, each at its own particular temperature, for which stable equilibrium of that crystal structure occurs. Generally two such different crystalline forms are all that are possible within the life-range of temperature of the substance, but instances have already been given in which three and even four distinct forms are known of one and the same chemical substance. Such a substance will thus present two or more different "solid phases," to adopt the language of physical chemistry, each characterised by a distinct crystalline form, with specific elementary space-lattice cell both as regards symmetry and dimensions, and specific optical and other physical properties. The conversion of one form into

another occurs sharply at a specific temperature, the pressure remaining sensibly the same, and the change of properties is likewise sudden and discontinuous. The phenomena of supercooling and superheating are not at all rare, however, in connection with this critical conversion-temperature, just as in the case of the melting point.

Very many other cases of polymorphism have been described, but the greater number have been proved not to be true cases of polymorphism, that is, of the development of two or more distinct structures with different space-lattices, by the same absolutely identical chemical molecules; they have, instead, proved to be cases of chemical isomerism, the two or more supposed "varieties" corresponding in reality to two or more different chemical molecules of distinctly different constitution, although composed of the same number and kind of atoms. As time goes on one after another of the substances formerly regarded as polymorphous, especially organic compounds, becomes removed from the list, the two or more forms having been eventually shown to be due to isomerism, tautomerism, or polymerism, so that it would appear that the list of truly polymorphous substances cannot be a very long one.

In order to be quite clear as to the meaning of these various terms, they are defined as follows: **Isomeric** (from *ἰσομερής*, "composed of equal parts") substances are such as possess the same empirical chemical composition, that is, the same number of atoms of the same chemical elements in the simplest formula (indivisible by any common factor) capable of expressing the composition of the substance, and which are yet quite different substances by virtue of one or other of the following facts, which discriminate between two distinct kinds of isomers. (1) The real constitution is only expressed by one or more of the isomers being a multiple or multiples of this simple empirical formula, and a different multiple in the case of each isomer, for instance acetylene C_2H_2 and benzene C_6H_6; the isomerism in this case is of the type specifically designated as *Polymerism*. Polymeric substances have the same percentage composition but different molecular weights. A special case of polymerism is the allotropy of an element. (2) The difference is due to differences in the arrangement of the atoms in the molecule, that is, to differences in molecular constitution, the two isomers possessing the same percentage composition and the same molecular weight. This type of isomerism is known as *Metamerism*, and a good example is afforded by the two substances of the empirical formula C_3H_7Br, to which correspond the two quite different substances propyl bromide $CH_3.CH_2.CH_2Br$ and isopropyl bromide $CH_3.CHBr.CH_3$. The term metamerism is, however, restricted by some authors to isomers containing several different carbon groups held together by an atom of more than monad valency, such as ordinary ethyl ether $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O$ and methyl propyl ether $\begin{matrix}CH_3\\C_3H_7\end{matrix}\!\!>\!O$. When the two or more isomers are so readily convertible one into the other that their separation is a matter of great difficulty we have the phenomenon distinguished by the term *Tautomerism*; the best example is hydrocyanic acid HCN, which is

probably a mixture of the molecules NCH and CNH, which are mutually convertible at ordinary temperatures. The phenomenon is only observed in liquids or solutions. Latterly it has come to be customary to refer to the isomers of the two classes (1) and (2), above distinguished, simply as polymers and isomers respectively.

The main fact to be emphasised, therefore, as being definitely established, is that the polymorphous states of the same chemical substance only differ in their crystal structure and the properties dependent on that structure. Their difference ceases as soon as the crystals are melted, dissolved in a solvent, or evaporated; for the chemical molecules thereby liberated in the liquid or gaseous state are identical when the substances are truly polymorphous. Any differences then still persisting must obviously be due to something else than polymorphism, namely, to different properties and nature of the molecules themselves, of which the crystals had been formed; that is, the two kinds of crystals must have been those of chemical isomers, substances composed of the same number of atoms of the same elements, but arranged as differently constituted molecules, different chemical entities with quite different properties. They consequently behave crystallographically as different substances invariably do, namely, they possess quite different crystalline forms; the most that such different substances can show in the way of crystallographic similarity is possible morphotropy, that is isogonism, similarity of angles along one or two particular zones only. It often happens, however, that isomeric substances are very easily converted one into the other, and then give the same substance on fusion, and such a possibility has always to be borne in mind during the investigation.

It will be gathered from the foregoing that a prominent characteristic of polymorphous modifications of the same substance is the capability of becoming converted, by change of temperature only, one into the other, without either fusion, evaporation, or the intervention of a solvent. This direct conversion of one crystalline form into the other may be observed under the Lehmann heating microscope (Fig. 843, page 1172), which enables the crystals to be studied during change of temperature, on heating to a temperature higher than the ordinary or on cooling therefrom. It is then possible not only to study the form during the growth of the crystals, but also the optical properties throughout the experiment, especially in polarised light when one of the forms happens to be isotropic, as is not infrequent, and the other doubly refractive. It can also be determined which is the stable modification for the particular temperature, as this forms at the expense of the other variety.

The thermal crystallisation-microscope can also be used to discover whether two forms are polymorphous or isomeric. One of them is melted on the stage, and then during cooling of the liquid the latter is touched at two different places by a small crystal of each of the two different sorts of crystal in question. If both grow until they touch, and then one continues to grow at the expense of the other, a little rewarming being effected if necessary, the two sets of crystals are polymorphous forms of the same chemical substance. But if only one of them grows,

or, supposing both to grow, if the two crystallisations on mutually touching remain indifferent to one another even when the temperature is raised, the two sorts of crystals are chemical isomers. The variation of the temperature is essential, as some polymorphous pairs remain indifferent to each other at the ordinary temperature for very long periods of time, in some cases days and in others years (*e.g.* the apparently equally stable calcite and aragonite, trigonal and rhombic $CaCO_3$). Also the absence of traces of a solvent must be ensured, as certain isomers (tautomeric substances) are readily converted into one another on solution. Another method of distinguishing between polymorphs and isomers will be given later in this section (page 1263).

On the conversion of the polymorphous form A, which is stable at the lower temperature, into the other form B, which is stable at the higher temperature, a thermal change is manifested, and as a rule B possesses a greater specific heat and lower density than A. At the critical temperature of conversion A and B are in equilibrium, and this temperature exhibits a similar dependence on the atmospheric pressure to that exhibited by the melting point. That is, if on conversion of A into B expansion occur, the conversion-temperature increases with the pressure, in accordance with the same law as that which the melting point follows. The overstepping of the temperature either way without the conversion occurring, corresponding to superheating or supercooling in fusion experiments, is only possible so long as no trace of the other modification is present. When such a condition of supercooling or superheating obtains, that condition of the substance is said to be metastable, and mere contact with a particle of the other modification relieves the strain. The labile condition or limit is that for which spontaneous conversion into the other form stable for that temperature occurs. Near the conversion-temperature the ordinary rule for such cases prevails, namely, that there is greater rapidity of conversion the greater the distance from the critical temperature of conversion. But when the supercooling is considerable, viscosity or solidity begins to be effective in a counter sense, and eventually its effect becomes relatively so great that both varieties can exist side by side. Such a case is afforded by sulphur, and even more perfectly by calcium carbonate, the stable trigonal form calcite and the metastable rhombic form aragonite being notoriously both apparently stable and mutually indifferent at the ordinary temperature; it is only on considerable rise of temperature, to near the actual conversion-temperature, when the solidity is weakened, that aragonite shows any sign of becoming converted into calcite. According to Johnston, Merwin and Williamson [1] aragonite changes pseudomorphously into calcite at rates which increase with the temperature, and the change is nearly instantaneous at 470° C. At −100° the reverse change occurs.

The rhombic form of sulphur, which has the higher density and smaller specific heat, is stable up to 95·6°, at which temperature change to the monoclinic modification occurs with absorption of heat; on the converse happening, cooling below 95·6°, heat is evolved. The critical temperature

[1] *Amer. Journ. Sci.*, 1916 [iv.], *41*, 473.

95·6° can, however, be easily overstepped, if no trace of the monoclinic form be admitted, until the sulphur melts at 113·5°. If, however, the monoclinic form be produced, this does not melt until the attainment of 119·5°. Conversely, the monoclinic crystals which separate from the "melt," if all trace of rhombic sulphur be precluded, can be retained on supercooling even down to the ordinary temperature, without reconversion into the rhombic form. Then, however, soon afterwards, spontaneous conversion into that stable form begins and spreads rapidly throughout the mass, the condition being thus a labile one. No overstepping of the critical temperature of conversion ever occurs, however, if the other modification be present. If sulphur be melted in a perfectly clean vessel and then supercooled carefully, without disturbance, crystals of either variety can be obtained at pleasure, by touching the fused mass with a crystal of that variety; the rapidity of crystallisation of the rhombic form under these conditions is, however, many times as great (25 to 100 times) as that of the monoclinic variety. Monoclinic sulphur is more soluble in chloroform, benzene, and ether than the rhombic variety.

Another case of special interest is that of mercuric iodide, HgI_2, which separates from aqueous solution in red tetragonal crystals, and from the state of fusion or by sublimation as yellow rhombic crystals; the latter, on cooling, change spontaneously into an aggregation of the red crystals, which can again be converted into the yellow rhombic crystals by heating, the critical temperature of the change being 126·3° C. This point can be overstepped either way if all disturbance be avoided, and the yellow variety may, if kept perfectly still, be retained at the ordinary temperature; the moment these yellow crystals are touched by a solid body, however, say on scratching with the point of a needle or pin, they immediately become converted into the red variety. On the passage of the red into the yellow form a sudden expansion of volume occurs, with absorption of heat; and the specific heat of the yellow modification is smaller than that of the red form, corresponding to an evolution of heat which occurs when the yellow form changes by cooling into the red form. Mercuric iodide of either form vaporises rapidly in a vacuum, even at low temperatures. If a solid body be held in the vapour, yellow crystals are deposited on it if the body have a perfectly clean surface. But if it has previously been rubbed with red crystals in one place, and with yellow crystals in another place, there are deposited red crystals at the one place and yellow crystals at the other.

It is thus clear that it is pre-eminently the temperature which determines the formation of the polymorphous modifications of a substance, given time for any temporary effects of supercooling or superheating to pass away, and for the properties associated with the metastable and labile conditions to be fully effective. Hence, by crystallisation at different temperatures the different modifications of a substance can be obtained from solution in the same solvent. For instance, the salt sodium monophosphate $NaH_2PO_4 . H_2O$, with which Mitscherlich in the year 1821 first observed dimorphism, is deposited in the ordinary rhombic form on the cooling of a warm aqueous solution; but if the crystallisation occur

at lower temperatures the second unstable form, also rhombic but quite different to the other, is obtained. The conditions are here assumed to be the same as regards supersaturation, namely, crystallisation from a metastable solution. Another instance is calcium carbonate, which crystallises from a carbonic acid solution below 30° C., or when precipitated from cold solutions of soluble calcium salts by a soluble carbonate (both very dilute), in little rhombohedra of the ordinary stable trigonal form of calcite, as shown by the photograph of a dilute precipitation taken by the author under a very high power and reproduced in Fig. 867 ; whilst by the rapid cooling of a hot solution the rhombic aragonite separates, either alone if the temperature be over 70°, or mixed with calcite if between 30° and 70° C. This forms quite a beautiful microscope experiment ; for if a drop of the hot solution in which the precipitation

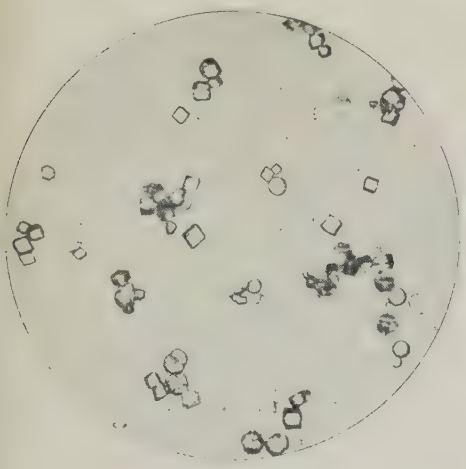


FIG. 867.—From a Cold Solution ; ⅛-inch Objective.

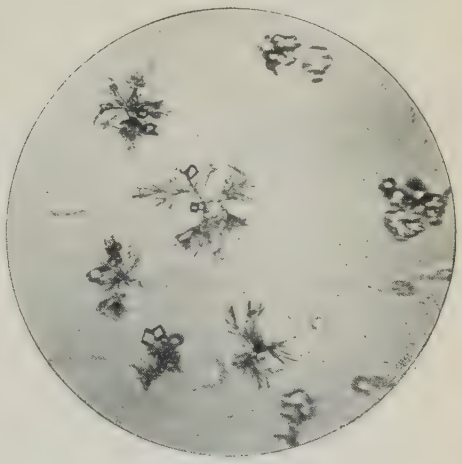


FIG. 868.—From a Hot Solution : ⅛-inch Objective.

Photomicrographs of Precipitated Calcium Carbonate.

is occurring be placed on a micro-slip, the feathery branching forms which aragonite takes when rapidly crystallised are at once produced, together with little rhombohedra of calcite which form more slowly and perch themselves here and there among the branches. A reproduction of a photomicrograph of such an actual preparation made by the author under a moderately high power is given in Fig. 868.

Calcite is the stable form of calcium carbonate, $CaCO_3$, at all ordinary temperatures. Under all ordinary conditions, therefore, aragonite tends to pass over into calcite, but the time required is very considerable, especially when dry. Hence, the well-formed crystals of aragonite formed naturally persist for all reasonable time when kept in dry places. They were probably formed in many cases by deposition from hot solutions, and in any case at a temperature higher than that at which calcite is formed.

The exact conditions obtaining on the passage from one polymorphous state or " phase " to another more stable one have been embodied by

Ostwald[1] in the principle that during such passage "it is not the most stable form which is attempted to be produced, but the form which lies next in stability," as defined by the three curves, plotted against vapour pressure (p) or solubility as ordinates and temperature (T) as abscissæ, which represent respectively the two solid phases or forms and the state of fusion. These three curves must intersect in pairs. As an example, suppose the case of sulphur be taken, represented in Fig. 869. The curve I is the vapour pressure curve of ordinary rhombic sulphur, and II that of the monoclinic variety, while the curve S is that of fused sulphur. The points m_{I} and m_{II} are the melting points of the two crystalline varieties, and c is the mutual conversion point. If liquid sulphur be under-cooled, we pass along the curve S from right to left through m_{II} and m_{I}, then through the metastable condition, and finally to x, where we arrive at the labile state, a solid form being then at once spontaneously produced. According to Ostwald's principle above stated, this solid form will not be the stablest form of sulphur, the rhombic I, but form II, the monoclinic, because the curve for this form II is nearer to x than is the curve I. Later on a point is reached at which curve II becomes representative of the labile condition, and the monoclinic form then changes finally into the permanent rhombic form I. It has already been shown that for sulphur $m_{\text{I}} = 113{\cdot}5°$, $m_{\text{II}} = 119{\cdot}5°$, and $c = 95{\cdot}6°$.

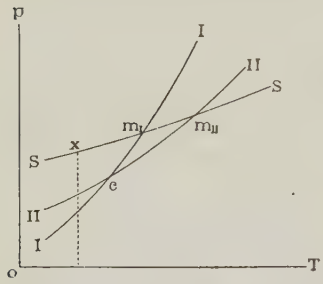


FIG. 869.—Vapour Pressure Curves of Rhombic (I), Monoclinic (II), and Fused (S) Sulphur.

Such bodies as sulphur, for which c in the diagram comes below the curve S, and for which the conversion can occur in either direction, being reversible, are termed by Lehmann "enantiotropic." There are other substances, however, such as benzophenone, $(C_6H_5)_2CO$, for which the point c comes above the S curve, and the conversion can only then proceed in one direction, that is, it is non-reversible; such substances are called by Lehmann "monotropic." Both enantiotropic and monotropic cases depend, however, on the same principle of Ostwald above stated, and represent the two possible modes of operation of the principle.

Two remarkable cases of monotropic dimorphism, which form very striking demonstration experiments, have been described by Chattaway and Lambert.[2] The substances in question are para-bromoacetanilide and 2 : 4-dibromoacetanilide, and their behaviour is almost exactly similar. On allowing a warm alcoholic solution to cool, fine needles of the labile variety separate, and so copiously that the containing vessel becomes completely filled with them. After some time, however, compact crystals of the stable form begin to grow at the top of the mass, at the expense of the needles, and eventually sink down to the bottom of the vessel.

Finally, as regards polymorphism, it is now possible to describe, with

[1] *Zeitschr. für phys. Chem.*, 1897, *22*, 306.
[2] *Journ. Chem. Soc.*, 1915, *107*, 1766.

fuller appreciation than would have been possible earlier in this section, the second method referred to on page 1259 of distinguishing between polymorphous and isomeric (including tautomeric) substances. The method is due to Sidgwick,[1] and depends on the fact that if a quantity of the less soluble of two polymorphous modifications of a substance be added to a saturated solution of the more soluble form the concentration will not increase, as the two modifications afford the same chemical molecules on solution; indeed, instead of increasing, the concentration will actually diminish, to a degree dependent on the difference of solubility of the two polymorphous varieties. But if two isomers be similarly treated, the addition of the less soluble crystalline solid does produce an increase of concentration, because two different chemical substances dissolve independently, each according to its own solubility, mutual interference being almost negligible. Sidgwick makes use of this principle to discriminate between polymorphs and isomers by determining the concentration, first for the two forms or different substances separately, and then for the two forms or isomers together, as the result of the addition of the less soluble one to the saturated solution of the more soluble one. If the two sets of crystals are dimorphous forms of the same substance, the result is somewhere intermediate between the results for the two separately; if they belong to different but isomeric or tautomeric substances, the result will be approximately the sum of the two. As a rapid means of estimating the concentration, Sidgwick employs the ordinary Beckmann process of determining the depression of the freezing point of some suitable solvent, the cryohydric point, by the two solids, first taken separately and then together as described. If the solids are dimorphous modes of crystallisation of the same chemical molecules the cryohydric point for their mixture is intermediate between the cryohydric points for the two taken separately; but if they are isomers the cryohydric point for their mixture is below that for the more soluble substance, the depression being more or less the sum of the two separate depressions. The method has proved very trustworthy and valuable.

Pseudo-symmetrical Polysymmetry.—Certain substances which simulate a higher symmetry than they really possess exhibit the remarkable property of becoming actually converted into the second form of higher symmetry at a higher temperature. One of the most interesting cases is Potassium Sulphate, K_2SO_4, the rhombic crystals of which have been shown on page 511 to simulate hexagonal symmetry, a pseudo-hexagonal structure being both naturally developed, the prism angle being only 12′ short of 30°, and also even more perfectly produced by triple twinning. Now Mallard has observed that when potassium sulphate crystals are heated, a sudden change occurs between 600° and 650° C., into a truly uniaxial form. Similarly, Gossner has shown that monoclinic but pseudo-hexagonal sodium potassium sulphate, $K_3Na(SO_4)_2$, and the analogous chromate, $K_3Na(CrO_4)_2$, are converted on heating into a truly hexagonal form.

Such instances are better classed as polysymmetrical rather than polymorphous. For it is quite possible, and indeed highly probable,

[1] *Journ. Chem. Soc.*, 1915, *107*, 672.

that they are due to submicroscopic repeated (lamellar) twinning of the original form, rhombic or monoclinic in the two cases just mentioned. Especially likely is this to be the case inasmuch as the change begins to be apparent while the temperature is still rising, some considerable number of degrees below the critical temperature of conversion.

An excellent and somewhat remarkable new case of polysymmetry has been described by C. T. R. Wilson.[1] It is that of butyranilide, which crystallises in the rhombic system, but with a pronounced pseudo-tetragonal habit. On allowing the crystals to remain at rest they spontaneously undergo the slight rearrangement necessary to convert them into truly tetragonal crystals. On raising the temperature the reverse occurs. The explanation is that the truly tetragonal form reaches its limit of stability at 10° C., and if the solution from which crystallisation occurs be maintained at a temperature below 10° C. the crystals deposited are those of the truly tetragonal form.

Another interesting case of polysymmetry is that of Quartz. It is now well established that there are four distinct minerals composed of silica, SiO_2, namely, quartz, tridymite, cristobalite, and quartzine, Moreover, each of the first three of these mineral species exists in two forms, which are distinguished as α and β varieties. The change from the α form to the β form is fairly rapid when once the transition temperature has been overstepped, whereas the reverse change is slow and accompanied by much supercooling. These three mineral species can exist side by side indefinitely, except at high temperatures. The difference of rapidity of the transformation between the α and β forms is probably due to the essential difference in the processes of polymerisation and depolymerisation. The two kinds of quartz, α and β, are supposed to be composed of the same kind of chemical molecules, the transformation being due to a slight modification of the lattice, and the same may be said of tridymite. But cristobalite behaves differently; the higher the temperature at which it was obtained from amorphous silica, the higher is the transition temperature, the α form changing into β-cristobalite at temperatures ranging regularly from 220° to 274°, according as the temperature of formation had been between 1050° and 1600° C. According to Fenner,[2] to whom much of our later knowledge of this subject is due, the number of molecules of SiO_2 is probably in the order α-cristobalite, β-cristobalite, β-quartz, α-quartz. The α and β varieties of quartz are very similar in optical properties, and only differ appreciably in symmetry. Fenner appears to have proved conclusively that at temperatures above 1470° C. quartz, tridymite, and amorphous silica are converted into cristobalite; between 1470° and 870° quartz, cristobalite, and amorphous silica are similarly converted into tridymite; and below 870° tridymite, cristobalite, and amorphous silica have been converted into quartz. It is thus obvious that cristobalite is the high temperature form, tridymite the intermediate temperature form, and quartz the ordinary lower temperature form of crystallised silica.

[1] *Proc. Roy. Soc.*, A, 1914, *90*, 169.
[2] *American Journ. Science*, 1913, *36*, 331. *Journ. Soc. Glass Tech.*, 1919, *3*, 116.

Considering first Tridymite, this mineral crystallises in the rhombic system, in the bipyramidal holohedral class 8, with a pronounced pseudo-hexagonal habit. It occurs naturally in apparently hexagonal plates, and in triplets of these, hence its name. Artificially crystallised silica, from fused acid silicates for instance, also usually takes the form of tridymite. This is also the form of silica found in meteorites, quartz being unknown in them, a fact established by Maskelyne. Some confusion has been caused, however, by this meteoric tridymite having been named "asmanite." At a temperature of 130° according to Mallard, or in the interval 130° to 160° according to Steinmetz,[1] rhombic tridymite is converted into a truly uniaxial, probably hexagonal, form, and this form appears to be permanent up to a low red heat. The reverse change occurs with much supercooling, often down to 90°. The change is accompanied by a distinct alteration in volume.

Considering next Cristobalite, this mineral, according to Mallard, crystallises in what appear to be regular octahedra, but are really pseudo-cubic triplets of tetragonal crystals, of negative uniaxial optical character. They possess both low refractive indices, averaging 1·432, and small double refraction, 0·0005. At 175° they change suddenly into isotropic truly cubic crystals.

The characters of Quartz have been specified in some detail on pages 354 to 356, and it need only be recalled here that it crystallises in the trapezohedral class 18 of the trigonal system. As regards Quartzine, this mineral may prove to be identical with chalcedony, although there are some differences in character and appearance. Wallerant[2] has shown quartzine to be a micro-crystalline fibrous aggregation, or massive variety, of silica. The fibres are of biaxial character, probably triclinic and certainly not of higher than monoclinic symmetry. They are positively doubly refractive, and exhibit an optic axial angle $2V_a$ of 58°, and refractive indices for sodium light as follows: $\alpha = 1{\cdot}5325$, $\beta = 1{\cdot}5355$, and $\gamma = 1{\cdot}5435$. The fibres have their long dimension parallel to the acute bisectrix of the optic axial angle, and apparently this forms the only clear distinction from the microscopic fibres of which chalcedony is composed, the form of silica (apparently amorphous) which is produced when silica is deposited from aqueous solution. The amorphous character is only superficial, however, for even the gem varieties of chalcedony possess this micro-crystalline fibrous structure, namely, carnelian (translucent red), sard (brownish red), plasma (leek green), bloodstone and heliotrope (plasma spotted with jasper[3]), agate (banded and variegated chalcedony), and onyx (when the bands are parallel and flat).

Under certain circumstances the fibres of quartzine take up a regular arrangement about a trigonal axis, and Sohncke has suggested that the

[1] *Zeitschr. für phys. Chem.*, 1905, *52*, 449.

[2] *Bull. Soc. franc. min.*, 1897, *20*, 52.

[3] Jasper is not pure silica, but an intimately disseminated mixture of quartz with clay or hydrated oxide of iron, which confers on it its usual creamy opacity and the remarkable deep red of Siberian jasper, the rich yellow of the jasper from India or Asia Minor, and the reddish-brown and sage-green strips of the riband jasper from the Ural Mountains.

structure of quartz is that of a regular point system formed by the spiralwise superposition of layers of quartzine, on the same principle as the mica combinations of Reusch described on page 1102 It is highly interesting that the indices of refraction for sodium light calculated for such an assumption are : $\omega = 1{\cdot}543$, and $\epsilon = 1{\cdot}553$, the real indices of quartz being 1·5443 and 1·5534, practically identical with these calculated values.

Now, at the temperature of 570° Le Chatelier [1] found that both quartz and quartzine suffer sudden expansion, and a change of rate of alteration of density with temperature. Friedel [2] also found that at 600° the etch-figures on quartz are no longer trigonal trapezohedral but hexagonal. It has also been shown on page 445 that F. E. Wright has found that at 575° the curve of change of the primary interfacial angle (100) : (111) suffers a complete break. It is at this temperature that ordinary or α-quartz becomes converted into β-quartz, with but little change in appearance, the transparency being unaffected, and the optical activity persisting. It is not until the temperature of 1000° C. is reached that the further change to tridymite occurs. This fact is confirmed by the observation that silica crystallised from fusion always takes the form of quartz at temperatures up to a low red heat, but of tridymite if the temperature of the fused mass be over 850°. It would thus appear that the conversion of ordinary α-quartz into β-quartz is due to the formation of a truly trigonal trapezohedral crystal out of the quartzine-layers-structure. This is the most reasonable assumption capable of accounting for the complete change of certain physical properties with practically no change in symmetry and optical activity. These facts render this the most interesting of all known cases of pseudo-symmetrical polysymmetry.

Isogonism or Morphotropy.—A considerable number of closely related compounds, chiefly organic, have been shown to crystallise in forms belonging to the same system of symmetry, which exhibit close similarity in the angles of one or more specific zones, the other zones being, however, quite different. Occasionally, moreover, the system of symmetry is different, yet the prism zone, or some other well-marked zone, exhibits close similarity in the disposition and angular inclinations of the faces. In all such cases full isomorphism is clearly absent, and the substances are said to be "morphotropic" [3] or "isogonal," the latter term ("equi-angular") more correctly expressing the character of the relationship, and affording an obvious and immediately understood appellation.

Pasteur,[4] in the year 1848, observed several cases of specific zonal likenesses among closely related tartrates. Laurent,[5] in 1842, and again in 1845, had previously described certain other cases, notably naphthalene tetrachloride, $C_{10}H_8 . Cl_4$, and chloronaphthalene tetrachloride, $C_{10}H_7Cl . Cl_4$, which crystallise respectively in the monoclinic and rhombic systems, yet exhibit a very similar prism zone, the angles of which were 109° 0′ and 109° 45′ respectively. His work, however, was subjected to prolonged

[1] *Compt. rend.*, 1889, *108*, 1046, and *109*, 264.
[2] *Bull. Soc. fr. min.*, 1902, *25*, 112.
[3] From $\mu o \rho \phi \acute{\eta}$, "form," and $\tau \rho \acute{o} \pi o \varsigma$, "manner."
[4] *Comptes rendus*, 1848, *26*, 535.
[5] *Ibid.*, 1842, *15*, 350 ; and 1845, *20*, 357.

criticism, and was not accepted at its real value until the observations of Pasteur brought confirmation. For together with real cases of morphotropy Laurent had introduced others of a very doubtful character, and coined terms to describe them such as "hemimorphism" and "isomeromorphism," which were both very objectionable and misleading, and the former of which was already in use, as at present, as descriptive of a type of symmetry.

Real progress in the clear definition of isogonism was effected by P. von Groth in the year 1870, and the term "morphotropy" was introduced by him. He carefully measured the crystals of a considerable number of solid derivatives of benzene, and found that even although the crystal system is frequently different there is often a striking resemblance between one or more of the predominant zones. He began with benzene itself, C_6H_6, which crystallises in the rhombic system, with axial ratios $a : b : c = 0{\cdot}891 : 1 : 0{\cdot}977$. He then found that when one or two of the hydrogen atoms are replaced by hydroxyl, OH, groups the substances produced, phenol C_6H_5OH and resorcinol $C_6H_4(OH)_2$, also form rhombic crystals, and in the latter case, for which alone the axial ratios could be determined, they proved to be similar as regards $a : b$ but very different with respect to $c : b$, namely, $a : b : c = 0{\cdot}910 : 1 : 0{\cdot}540$. The three nitro-derivatives of phenol were then investigated, orthonitrophenol $C_6H_4 . OH . NO_2$, dinitrophenol $C_6H_3 . OH . (NO_2)_2$, and trinitrophenol $C_6H_2 . OH . (NO_2)_3$, and all were found to form rhombic crystals having the respective axial ratios $a : b : c = 0{\cdot}873 : 1 : 0{\cdot}60$, $0{\cdot}933 : 1 : 0{\cdot}753$, and $0{\cdot}937 : 1 : 0{\cdot}974$. The value of $a : b$ is thus again somewhat similar to that for benzene, while the $c : b$ ratio is different. Meta-dinitrobenzene $C_6H_4(NO_2)_2$ and trinitrobenzene $C_6H_3(NO_2)_3$ were also found to crystallise similarly with closely related $a : b$ ratios, the values of $a : b : c$ being respectively $0{\cdot}943 : 1 : 0{\cdot}538$ and $0{\cdot}954 : 1 : 0{\cdot}733$. Chlorination was found to produce a greater effect, the replacement of a hydrogen atom by a chlorine atom being frequently sufficient to lower the symmetry from rhombic to monoclinic; yet even in these cases the faces in the primary prism zone remained very similar, the variation in the angle (110) to ($1\bar{1}0$) being only 5°, from 93° 45′ to 98° 51′.

Groth[1] at a later period has used molecular volumes and topic axial ratios for his morphotropic comparisons in cases of more or less similar types of replacement, and draws special attention to the case of ammonium iodide NH_4I and its substituted homologous alkyl radicle derivatives, tetramethyl, tetraethyl, and tetrapropyl ammonium iodide, $N(CH_3)_4I$, $N(C_2H_5)_4I$, and $N(C_3H_7)_4I$. Ammonium iodide crystallises in the cubic system, in cubes, and with the cube cleavage. The space-lattice is, therefore, that of the simple cube. The density of the crystals is 2·501, the molecular weight is 143·83, and the molecular volume V is, therefore, 57·51. From this the edge dimension of the elementary cube cell of the space-lattice, that is, the topic axial value $\chi = \psi = \omega = \sqrt[3]{V}$, is 3·860. Tetramethyl and tetraethyl ammonium iodides form tetragonal crystals. The former possesses perfect cleavage parallel to the rectangular prism {100} and basal plane {001}

[1] *Einleitung in die chemische Krystallographie*, 1904, p. 31.

faces, the tetragonal equivalent of the cubic cleavage. It differs from the parent ammonium iodide in the different relative dimensions of the vertical c-axis as compared with the lateral axes a and b which remain equal, the difference being brought about by the enlargement of the two equal horizontal axes aa, the c-axis remaining unaltered by the replacement of the four hydrogen atoms by four methyl groups. The tetragonal crystals of tetraethyl ammonium iodide, however, do not show the same cubo-tetragonal type of cleavage, but that the substance belongs to the same morphotropic series is shown by the regular accretion of molecular volume for the three substances, and also by the regular increase of the topic dimensions χ and ψ, while ω for the direction of the c-axis again shows but little change. The substitution of organic radicles more complicated than methyl CH_3 and ethyl C_2H_5, however, propyl C_3H_7 for instance, upsets the equilibrium of the system much more, a difference now becoming apparent between the two horizontal axial dimensions, and the c-axis becoming elongated; the volume also becomes more considerably augmented than for the methyl and ethyl substitutions. The following table will render this clear:

NH_4I.	$N(CH_3)_4I$.	$N(C_2H_5)_4I$.	$N(C_3H_7)_4I$.
$V = 57{\cdot}51$	108·70	162·91	235·95
$\chi = 3{\cdot}860$	5·319	6·648	6·093
$\psi = 3{\cdot}860$	5·319	6·648	7·851
$\omega = 3{\cdot}860$	3·842	3·686	4·933

From these observations Groth concluded that the substitution of the CH_3 and C_2H_5 groups for hydrogen in the crystal-structure of ammonium iodide occurs in one of the cube planes of the latter, which thereby takes up the character of a tetragonal basal plane. He imagined the iodine atoms as forming a cubic space-lattice, with a nitrogen atom at the centre of the cube, while the hydrogen atoms were situated between the iodine and nitrogen atoms in the four tetrahedra normals. The replacing carbon and hydrogen atoms would (until the alkyl radicle group became too heavy and complex) then all lie in the horizontal plane, and this would cause a tearing apart of the iodine atoms in the four horizontal directions.

Vegard[1] has recently (1917) carried out the X-ray analysis of these interesting compounds, and finds that Groth's suppositions are not altogether substantiated by the facts of structure elucidated, the morphotropic relationship not being explained by substitution alone; for the iodine and nitrogen lattices are not merely quite differently arranged, but the structure in the two cases contains a different number of elementary iodine and nitrogen lattices. The NH_4I lattice is composed of 4N, 16H and 4I lattices or $4(NH_4I)$, while $N(CH_3)_4I$ has 2N, 8C, 24H and 2I lattices or $2[N(CH_3)_4I]$, that is, the structure is based on a unit of four molecules in ammonium iodide (or half a molecule in the small cube which is one-eighth of the large cube-cell) and two molecules only in the substituted iodide.

[1] *Phil. Mag.*, 1917, *33*, 395.

Vegard finds the atoms to be arranged in face-centred-cube lattices, not in simple cubes, and the N and I lattices are relatively arranged like the sodium and chlorine in rock salt. The reflecting power of hydrogen is so small that certainty is difficult, but most probably the four atoms belonging to each molecule are situated at the corners of a tetrahedron with the N-atom in the centre, the lines from the N-atom to any of the four H-atoms being parallel to one of the diagonals of the cubic lattice A photograph of a model is reproduced in Fig. 870.

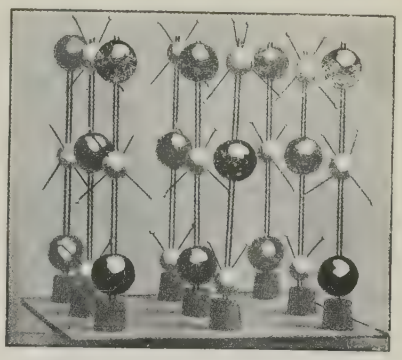


FIG. 870.—Structure of Ammonium Iodide.

The H lattice is, of course, the same in size as the lattices of I and N, and this necessitates that all the tetrahedra are parallel, and the symmetry is hemihedral of class 31 (hexakistetrahedral).

The tetragonal structure of $N(CH_3)_4I$ is much more complicated. The corners of the tetragonal cell appear to be formed by I-atoms, and there is an N-atom at the centre of the cell, and *vice versa* an I-atom at the centre of each N cell. There is also, however, another I-atom on the vertical axis passing through

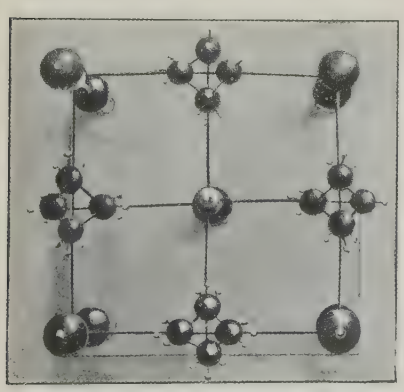


FIG. 871.

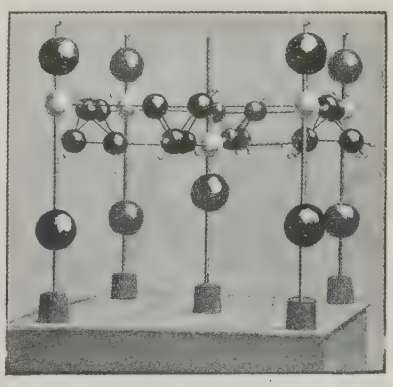


FIG. 872.

Structure of Tetramethyl Ammonium Iodide.

the centre, at a definite distance from the N-atom. Also there is an N-atom on each vertical edge of the cell at a similar distance from the I-atom at the nearest corner-termination of that edge. The arrangement will be seen from the two photographs of models, Figs. 871 and 872, which also show the C-atoms arranged in groups of four at the corners of a tetragonal sphenoid (two of the four only belong to the structural unit shown, the two others belonging to the neighbouring one in each case). The H-atoms are also shown very small in the models, and they lie at the

corners and centres of alternate edges of the same tetragonal cell as that on which the C-atoms lie, in the middle of the other alternate edges. The somewhat startling result is afforded, however, that although within the volume equal to that of the elementary cell of the lattice of $N(CH_3)_4I$ there are only two molecules, whereas the lattice cell of NH_4I contains four molecules, yet one molecule of the former is found to occupy approximately the same space as two molecules of the latter, the absolute height of the tetragonal prism of the former being very nearly the same as that of the cube of the latter, as indicated also by the topic axial ratios. Thus the topic axial ratios for ammonium iodide NH_4I and its methyl-substituted compound $N(CH_3)_4I$ are very similar, and yet the molecules are arranged in quite different lattices. Vegard therefore concludes that the morphotropic relations supposed to exist by Groth between NH_4I and $N(CH_3)_4I$ have no existence, and that the topic axes of morphotropic bodies are not strictly comparable. The topic axes of isomorphous substances only are strictly comparable.

Groth[1] has more recently pointed out morphotropic resemblances, as indicated by more or less regular changes in the topic axial ratios, between certain organic compounds of cyclic constitution, namely, the imides of succinic acid, of dimethyl succinic acid and of tetramethylsuccinic acid. He regards this as another case of morphotropic regularities due to a regular type of chemical replacement.

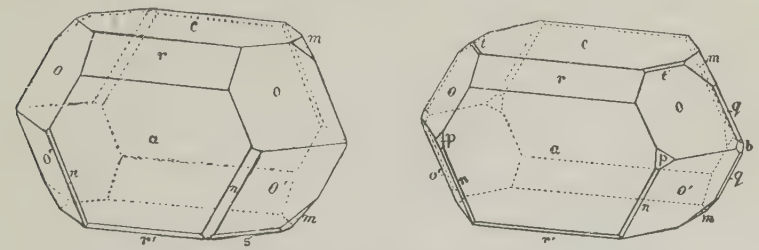
A case which appears to be intermediate between one of morphotropy and one of isomorphism was described by the author[2] in the year 1890. It was a homologous series of organic substances differing by CH_2, the methyl CH_3, ethyl C_2H_5, and propyl C_3H_7 derivatives of triphenylpyrrholone. The case is somewhat complicated by polymorphism, for each member is dimorphous, and indeed one of them and possibly all three trimorphous, only two forms, however, being readily prepared. That these varieties are polymorphous forms and not isomers was proved by the direct manner in which one variety can be obtained from the other by merely altering the conditions (especially temperature) of crystallisation from the same solvent.

Methyl triphenylpyrrholone, $(C_6H_5)_2C-CH$, $CO\ C\cdot C_6H_5$, $N\cdot CH_3$, crystallises in trigonal rhombohedra and in triclinic prisms, a crystal of the former having been shown in Fig. 398 on page 503, and one of the latter in Fig. 47 on page 98, and its forms and elements given as an example of a triclinic crystal of class 2 on page 278. The ethyl compound (in which the CH_3 at the bottom of the above formula is replaced by C_2H_5) crystallises in similar and apparently isomorphous triclinic prisms, exactly like Fig. 47, and also in monoclinic crystals of the type already shown in Fig. 772 on page 1063 and reproduced at (*a*) in Fig. 873. A rhombic form of the ethyl compound was also once produced, but lost on attempting to recrystallise, the conditions for its formation not having been ascertained. The propyl compound (C_3H_7 replacing the CH_3) crystallises also in monoclinic crystals isomorphous to all appearance with those of the ethyl compound, a typical

[1] *Zeitschr. für Kryst.*, 1915, *54*, 498. [2] *Journ. Chem. Soc.*, 1890, *57*, 714.

crystal being represented at (*b*) in Fig. 873. Propyl triphenylpyrrholone also assumes the form of rhombic crystals, like those once obtained of the ethyl compound.

That the close similarity of the triclinic forms of the methyl and ethyl triphenylpyrrholones, and of the monoclinic forms of the ethyl and propyl compounds, is not to be distinguished from true isomorphism is shown by the fact that the angular differences are of the same small order as the author has shown to be characteristic of isomorphous compounds crystallising in the lower systems of symmetry ; the angular differences between the monoclinic forms of the ethyl and propyl triphenylpyrrholones were smaller than those between the triclinic forms of the methyl and ethyl compounds, the differences thus diminishing as the symmetry becomes higher, a principle which has already (page 1231) been shown to be generally observed. The average and maximum differences between the triclinic substances are 2° 19′ and 4° 34′, and those between the monoclinic substances are 1° 53′ and 3° 42′. The number of different angles compared was 23 in the former case and 22 in the latter.



(*a*) Ethyl. (*b*) Propyl.

FIG. 873.—Monoclinic Forms of Ethyl and Propyl Triphenylpyrrholone.

The monoclinic ethyl and propyl compounds are also remarkably similar optically, a point which is emphasised by the very unusually large amount of dispersion of the optic axes which is exhibited by both. In the case of the ethyl compound it is so large that the phenomenon of crossed-axial-plane dispersion is shown, which has been described in Chapter XLIX. and illustrated in Fig. 773. The optic axial interference figure in convergent polarised white light is an exceptionally beautiful one (*f* in Fig. 773), very similar to that given by brookite (rhombic TiO_2) without the drawback of the deep red colour of the crystals of brookite, those of ethyl triphenylpyrrholone being almost perfectly colourless (very faint yellow). The optic axes as seen in air are separated 32° 30′ in a plane perpendicular to the symmetry plane for red lithium light (*a* in Fig. 773), and in the symmetry plane itself 21° 50′ for green thallium light (*d* in Fig. 773), a total dispersion within these wave-lengths of 54° 20′. For light of the wave-length 0·000575 mm. in the greenish-yellow the uniaxial figure of circular rings and a rectangular cross is exhibited (*c* in Fig. 773). The propyl compound shows 11° of dispersion of the optic axes within the same limits of wave-length, in one and the same plane. This large dispersion, resulting in great sensitiveness to change of wave-

length in the illuminating light, is due to the very low double refraction which both compounds possess, that of the ethyl compound being so excessively small as to render the sensitiveness extreme, resulting in the crossing of the optic axial planes and the passing through the stage of apparent uniaxiality, in accordance with the principles fully explained in Chapter XLIX.

Enantiomorphism.—It was shown in Chapter IX. (pages 131 to 133) that those substances which crystallise in forms belonging to the eleven crystal classes which possess no planes of symmetry, either simple or alternating, develop two varieties of crystals, which are complementary to each other as an object is to its mirror-image, or as a right-hand glove is to its left-hand fellow. Such pairs of complementary crystals are termed "enantiomorphous," from ἐναντίος, "that which is over against, opposite," and μορφή, "shape," the shapes or crystal forms being of opposite character. Moreover, many (those which possess a screw structure) of these substances exhibit optical activity, that is, the property of rotating the plane of polarisation of polarised light, one variety rotating it to the right, hence called the right-handed or dextro variety, and the other kind rotating it to the left and therefore termed left-handed or the lævo variety. Optically active substances invariably belong to one or other of the eleven classes of crystal symmetry in question, and therefore exhibit enantiomorphism. The classes referred to are the following: The asymmetric class 1 of the triclinic system, the sphenoidal class 4 of the monoclinic system, the bisphenoidal class 6 of the rhombic system, the pyramidal classes 16, 9, and 23 of the trigonal, tetragonal, and hexagonal systems, the trapezohedral classes 18, 11, and 24 of the same three respective systems, and the tetrahedral-pentagonal-dodecahedral and pentagonal-icositetrahedral classes 28 and 29 of the cubic system. But as there are point systems conforming to one or other of these eleven classes yet which do not possess screw axes (which appear to be the cause of the ability to rotate the plane of polarisation of light waves), there are some substances crystallising in one or other of these classes which are not optically active; barium nitrate, $Ba(NO_3)_2$, is an example, crystallising in the cubic class 28 as illustrated in Fig. 130 on page 169. The optical activity being due to the presence of a helical structure, or (otherwise expressed) to a structure exhibiting the possibility of screw coincidence movements, and screws being of two varieties, right-handed and left-handed, the optical activity, like the enantiomorphism of the crystals, may be either left-handed or right-handed likewise, and the same substance may, and usually does, develop both varieties, like quartz or tartaric acid, for instance.

Any substance, therefore, which exhibits right- or left-handed rotary power over the plane of polarisation of light is invariably found, if it be capable of crystallisation, to produce two varieties of crystals, one variety being the mirror-image counterpart of the other, and each variety being responsible for one kind of optical rotation. In many cases not only are the crystals optically active, but also their solution in a solvent, which indicates that the chemical molecules themselves are enantio-

morphous. Sometimes, however, the optical activity is destroyed by the act of solution, in which cases it is clear that the crystal structure only is enantiomorphous and not the chemical molecules of the substance. Sodium chlorate $NaClO_3$ is a case of this kind, belonging, like barium nitrate, to class 28 of the cubic system.

The dextro and lævo varieties of the substance are thus distinguished by their right- or left-handed enantiomorphous crystal structure. They are alike in their physical properties, such as density, melting point, thermal expansion, elasticity, refractive indices, optic axial angle, and cleavage. The crystal angles are identical as regards all those forms (using "form" in its strict sense, to include faces of equal symmetry value) which the low class of symmetry possesses in common with the holohedral class of the same system. The crystallographic difference becomes apparent with respect to those other forms which are peculiar to and characteristic of the specific low class, and which comprise a half or a quarter of the faces only of the holohedral forms, and were therefore formerly called hemihedral or tetartohedral. For the two or four complementary forms of any such pairs or sets together making up the holohedral form are never developed in common by the two varieties, the right or positive form being present on and characteristic of one optical variety, and the complementary left or negative form being characteristic of the other. It frequently happens, however, that a particular crop of crystals of an enantiomorphous substance shows only the main primary holohedral forms common to both the holohedral class and the lower symmetry class, and no trace of the particular class forms. In such cases the enantiomorphous character is revealed by (1) the optical activity of the crystals or their solutions (this fails in the cases like barium nitrate); (2) the etch-figures afforded by a trace of a solvent, the lack of holohedral symmetry being usually clearly revealed by the nature of the figures; or (3) the pyro-electric properties developed on warming a crystal and allowing it to cool, the right-handed variety developing opposite electric polarity to the left-handed variety, as revealed by dusting with Kundt's powder (sulphur and red lead), the sulphur going to the positively electrified parts and the red lead attaching itself to the negative parts (see Figs. 916-920 in Chapter LIX. on the Electrical Properties of Crystals). It will be obvious, therefore, that no crystallographic investigation of a new substance can be considered complete, or anything like adequate, which deals only with a single crop of crystals; the examination of a considerable number of crops is essential, and, in the case of an enantiomorphous substance, will usually eventually reveal crystals exhibiting the faces of the distinguishing right or left forms. Moreover, when, as not infrequently happens, certain crystals show both complementary forms of a particular pair, there are usually striking differences in the reflecting power of the faces of the two, those of one form being brilliant and affording excellent signal reflections, while those of the other are dull, curved, or rough.

Enantiomorphism and Optical Activity. — The connection between optical activity and enantiomorphism of crystalline form was first

discovered by Pasteur[1] in the year 1848, as the result of his investigation of tartaric acid. This well-known substance, $C_4H_6O_6$, possesses the constitution $\begin{matrix}CHOH\ .\ COOH\\ |\\ CHOH\ .\ COOH.\end{matrix}$ It was isolated in 1769 by Scheele, as the result of the first research of that distinguished chemist. In 1826 Gay Lussac investigated a very similar substance which had been found in grape juice at Thann in Alsace. His results, however, were indecisive, as were also those of Gmelin, who examined the substance in 1829, and who gave it the distinctive name Traubensäure, acid of grapes. Later, Berzelius tackled it, and went so far as to prove that its empirical formula was certainly $C_4H_6O_6$, like that of tartaric acid, but that it differed in essential properties from Scheele's tartaric acid. Biot next studied its optical properties, and showed that whereas Scheele's tartaric acid is optically active, rotating the plane of polarisation to the right, this new substance, which has since been known in this country and France as racemic acid, is without action on polarised light. Both the solid crystals of Scheele's tartaric acid and their aqueous solution rotate the plane of polarisation to the right, in the case of the crystals (as determined many years afterwards by Dufet) to the extent of 11·4° for sodium light and a plate one millimetre thick (see page 1111).

Pasteur's discovery in 1848 was a great advance, for he showed that a new principle was involved, that of physical isomerism, and that racemic acid is a molecular compound of two physical isomers, one, the dextro variety, being Scheele's tartaric acid, and the other being an exactly complementary lævo variety, which he succeeded in isolating. Ordinary well-known chemical isomerism occurs, as already stated, when two substances expressed by the same empirical chemical formula possess a totally different chemical constitution and properties, such as, for instance, normal propyl chloride $CH_3\ .\ CH_2\ .\ CH_2Cl$ and isopropyl chloride $CH_3\ .\ CHCl\ .\ CH_3$, both of which have the empirical formula C_3H_7Cl. Physical isomerism, however, occurs when the constitution as well as the empirical composition is the same, but the atoms or groups of atoms are differently disposed in space. It has now been established, largely by the stereometric work of Van 't Hoff and Le Bel, that the optical activity of carbon compounds is frequently connected with (although the condition is not essential, as will subsequently be proved) the possession of a so-called "asymmetric" carbon atom, that is, an atom of carbon saturated as regards its four valency "bonds" by being connected with four quite different elements or groups. Tartaric acid possesses two such asymmetric carbon atoms, namely, those in the two CHOH groups; for each is connected by one bond with a hydrogen H atom, by another bond with the oxygen atom of a hydroxyl OH group, by a third bond with the carbon atom of a COOH group, and by its fourth bond with the other asymmetric carbon atom and thereby with the whole other half-molecule, CHOH . COOH. Now the groups of atoms in one half-molecule may be either symmetrically arranged with respect to those of the other semi-molecule, or they may be differently

[1] *Ann de Chim. et Phys.*, 1848, *24*, 28 and 38

disposed. If they are symmetrical the whole molecule will be optically inactive, but if they are unsymmetrical they may be so in either a right-handed or a left-handed manner, the two arrangements being related to each other as an object and its image in a mirror. This is the explanation of the two optically active varieties of tartaric acid, and racemic acid consists of a molecular compound, more or less loose, of equivalent molecular proportions of these two varieties, the one exactly neutralising the other as regards optical activity. The molecules of each variety being enantiomorphous, their solutions are optically active; and in building up crystals the homogeneous structures produced naturally possess a helical nature, so that the crystals also are optically active. Moreover, to complete the proof, Pasteur[1] discovered a fourth modification of tartaric acid, which is not only optically inactive like racemic acid, but, unlike the latter, cannot under any circumstances whatever be split up into right- and left-handed components. Other workers have since shown that there are even three varieties of this truly inactive modification of tartaric acid, as there are three ways in which the symmetrical internal arrangement can occur within the chemical molecule; this is termed internal compensation, racemic acid being a case of external compensation, that is, external to the molecule.

The facts are best stated as follows: If the compound (molecule) has no axis of symmetry of the second order (see page 602), and no symmetry plane, nor a centre of symmetry, we may obtain two enantiomorphous varieties or isomerides. That is, if the stereometrical configuration of the atoms in the molecule possesses only first order axial symmetry, the substance is resolvable into two enantiomorphous components. But if a second order symmetry property be found, the compound will not be capable of such resolution, even although several asymmetric carbon atoms be present. Such a case is meso-tartaric acid, Pasteur's fourth, inactive, variety of tartaric acid, which has the two starred asymmetric carbon atoms, and in which one half of the molecule is the mirror-image of the other half, the compound thus possessing a plane of symmetry, a second order symmetry element. Thus no enantiomorphism of stereometrical arrangement can ever occur, and be represented in the actual solid by two crystalline varieties or complementary antipodes, when the configuration of atoms as a whole shows any symmetry element of the second order.

```
COOH
|
*CHOH
|
*CHOH
|
COOH,
```

Racemic acid, the resolvable apparently inactive tartaric acid, can be readily obtained by simply crystallising from a mixed aqueous solution of equivalent molecular quantities of dextro and lævo tartaric acids. Pasteur showed that on mixing the two equivalent solutions heat is evolved, a sure sign of chemical combination, even if only molecular. In this external compensation the two kinds of enantiomorphous molecules are regularly distributed throughout the crystal structure, which is that of the new double molecule as an entity, and the resultant crystals consequently are quite different from the monoclinic optically active tartaric

[1] *Ann. de Chim. et Phys.*, 1850, *28*, 56; *Comptes rendus*, 1853, *37*, 162, and 1858, *46*, 615.

acids, and indeed are not anhydrous like the latter, but include a molecule of water of crystallisation; racemic acid, $C_4H_6O_6 . H_2O$, forms triclinic crystals of the pinakoidal class 2, of specific gravity 1·788, that of the two monoclinic optically active tartaric acids being 1·759. Once put together to form racemic acid as just described, the two optically active varieties cannot be directly recovered. But if the acid be neutralised partly by soda and partly by ammonia, by adding ammonium hydrate to a solution of the readily obtainable hydrogen sodium racemate, the salt sodium ammonium racemate $\begin{matrix}CHOH . COON_a \\ | \\ CHOH . COONH_4\end{matrix}$ is obtained on crystallisation, and

Pasteur obtained a number of crops in which all the crystals were hemimorphic, some crystals being right-handed and others left-handed. On collecting a number of each kind separately, and recrystallising them apart, the right- or left-handed character and similar handed optical activity were found to be retained, and on converting them into the very slightly soluble lead salts by the addition of a soluble lead salt, and then decomposing the two precipitated lead salts with sulphuretted hydrogen, ordinary dextro tartaric acid was obtained from the one and the lævo acid from the other; indeed, this was the method by which Pasteur first isolated lævo tartaric acid. Also, on momentarily touching a metastable solution of ammonium sodium racemate (saturated at 28° C. and allowed to cool to the ordinary temperature) with a crystal of either the right- or the left-handed salt, the crop of crystals obtained consisted entirely of that variety, so long as any of that kind remained in solution, after which the other salt began to be deposited.

It has been shown on page 255 that ordinary dextro and lævo tartaric acids crystallise in the sphenoidal class 4 of the monoclinic system (monoclinic-hemimorphic), and two typical crystals are illustrated in Figs. 211 and 212 on page 255. It will be immediately recognised that the two forms are related as mirror-images. Some of the principal (primary) crystal angles of the two kinds are identical, but owing to the absence of the symmetry plane in this class 4 the crystals of the two varieties are complementarily hemimorphic as regards the faces at the two ends of the remaining digonal axis *b*, the 4-faced clino-prism {011} of the holohedral class being divided into two 2-faced forms, the right clino-prism {011} and the left clino-prism {011}, and the former is characteristic of dextro tartaric acid and the latter of the lævo acid.

Pasteur's Law, as the principle discovered by him has come to be termed, may be stated more or less as originally propounded by him as follows: (*a*) If the atoms of a chemical molecule be "dissymmetrically" arranged, this molecular "dissymmetry" implies the possibility of the existence of two oppositely complementary configurations of the molecule. Both varieties have the same chemical properties, and they are endowed always with equal but oppositely directed rotatory power. The presence of molecular dissymmetry therefore reveals itself by this rotatory power of the molecules and is wholly determined by their chemical constitution. (*b*) When the atoms of a chemical molecule are dissymmetrically arranged,

the fact is at the same time betrayed by the occurrence of the two varieties in complementary non-superposable crystalline forms, possessing screw axes of opposite winding.

The stereometric work of Van 't Hoff and Le Bel consisted chiefly in showing that a molecule is "dissymmetrical" when the dominating carbon atom, the four valencies of which can be stereometrically represented as situated at the four corners of a tetrahedron, has its four valencies asymmetrically satisfied, that is, by four different atoms or radicle groups.

In this research Pasteur made a further very fruitful observation, namely, that when the spores of a ferment, *Penicillium glaucum*, are added to a solution of racemic acid containing traces of phosphates (which appear necessary to the life of the organism), the organism eats up and destroys the dextro component of the molecular compound, the lævo component being unattacked so long as any dextro is left. If, therefore, the fermentation be stopped at the proper time the solution will contain only the lævo component, which can be crystallised out practically pure.

The crystals of dextro and lævo tartaric acid exhibit very clearly the pyro-electric properties of enantiomorphous crystal varieties, the two ends of the digonal axis *b* behaving oppositely when the crystals are warmed and allowed to cool; if they are tested during the cooling process by being sprinkled with Kundt's powder (S and Pb_3O_4) from a muslin bag, the end on which the clino-dome faces are present will show the development of positive electrical excitation, the negatively electrified yellow sulphur particles adhering to it, while the other end, developing negative excitation, will be found to have attracted the red lead. These facts are illustrated in Fig. 918 in Chapter LIX.

Racemism and Pseudo-Racemism.—The phenomenon of the molecular combination of two enantiomorphous varieties of a substance (physical isomers), first met with in tartaric acid, has since been observed with respect to the physical isomers of many other substances, and has come to be termed "racemism." The use of ferments in a similar manner to that made of them by Pasteur has also become very common, and almost general, for the isolation of one of the two separable varieties, as the ferment invariably shows a preference for, and a greater ability to destroy and assimilate, one variety rather than the other. Racemic substances always crystallise differently to the optically active components, because in the former the latter are chemically combined, although the affinity may be one of the lesser degree known as "molecular combination." The resulting substance acts in any case as a new and quite different entity, which builds up a different crystal structure. There may occasionally be morphotropic (isogonal) resemblances along one or more zones, but there can be no general similarity.

Benzilidene camphor, $C_{10}H_4O \cdot CH \cdot C_6H_5$, affords a particularly clear case of the difference between the racemic and optically active forms. The racemic molecular compound of the two active forms, obtained by the evaporation of a solution of equal molecular quantities of the dextro and lævo active varieties, forms monoclinic prismatic crystals which melt

at 73°. The two active varieties crystallise separately in rhombic bisphenoidal crystals, class 6, which do not melt until 98°, and are obviously utterly different from the monoclinic racemic crystals.

A very curious and interesting phenomenon, which is akin to that of pseudo-symmetry referred to on page 1263, is frequently observed owing to the repeated microscopic or even sub-microscopic twinning of a pair of enantiomorphous physical isomers, and is known as "pseudo-racemism." The result of such exceedingly fine lamellar twinning is the production of a crystal which is apparently holohedral, showing both enantiomorphous forms, that is, the development of both sets of distinctive hemimorphic forms. Microscopically thin layers of the right- and left-handed varieties are alternated, just as in the case of amethystine quartz, which forms a gross but excellent illustration; right- and left-handed quartz are repeatedly alternated in layers visible to the naked eye, in the purple sectors (Fig. 413 on Plate III., facing page 510). These alternate layers are exquisitely revealed in polarised light by their different and very brilliant colours, as described on pages 509 and 510, and illustrated in Figs. 414 and 415 on Plate III., and Fig. 416 on page 510. In consequence the crystal structure simulates a higher symmetry than the individual laminæ possess, as is so commonly the result of laminated twinning. A number of pseudo-racemic organic substances have been described by Kipping and Pope.[1] They define a pseudo-racemic substance as "an intercalation of an equal, or approximately equal, proportion of two enantiomorphously related components, each of which preserves its characteristic type of crystalline structure, but is so intercalated with the other as to form a crystalline individual of non-homogeneous structure. A solid racemic compound, on the other hand, may be defined as a crystalline substance of homogeneous structure which contains an equal proportion of two enantiomorphously related isomerides. . . . An inactive externally compensated substance, which closely resembles its active isomerides crystallographically, is to be considered as pseudo-racemic, whereas when the contrary is true it is to be regarded as racemic."

Sobrerol, $C_{10}H_{18}O_2$, forms a good example of a pseudo-racemic substance. The crystals of the various varieties were investigated by Miers and Pope.[2] The two optically active varieties form monoclinic sphenoidal crystals, class 4, a representative specimen of which is shown in Fig. 874. The crystals are very soft, being readily bent. The basal plane $c\{001\}$ is a plane of gliding. When an alcoholic solution of equal molecular proportions of the two is allowed to crystallise rhombic pseudo-racemic crystals are formed, one of which is shown in Fig. 875. The ratio of the axes and the optical properties of this rhombic form are nearly identical with those of

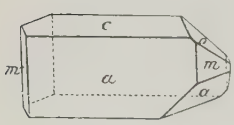


Fig. 874.
Crystal of Dextro-sobrerol.

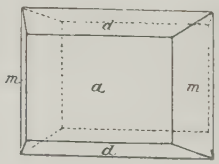


Fig. 875.
Crystal of Inactive Sobrerol.

[1] *Journ. Chem. Soc.*, 1897, *71*, 989.

[2] *Zeitschr. für Kryst.*, 1892, *20*, 321.

the two active components. The specific gravity of all three is identical, but the melting point of the rhombic pseudo-racemic crystals is different from that of the two active varieties, for the reason that on heating a truly racemic form is produced.

The Essential Condition for Existence of Optical Antipodes.—The most recent researches, especially those of F. M. Jaeger,[1] lead to the conclusion that the unique and all-sufficing condition for the production of optical isomerism, the possibility of the existence of two optical antipodes, is that the molecule does not possess an axis of the second order. A figure can only differ from its image when it possesses as its elements of symmetry only simple axes of rotation. Neither the absence of a plane of symmetry nor that of a centre of symmetry suffices for the production of a case of optical isomerism ; there must also be the absence of an axis of the second order. For as soon as such a second order axis is present, the configuration becomes such as should be identical with its own image, and therefore enantiomorphism cannot occur. Hence the only indispensable condition for the existence of optical antipodes is that the elements of symmetry present shall be those of the first order only, ordinary digonal, trigonal, tetragonal, or hexagonal rotation axes. The presence of an asymmetric carbon atom, or even of several such atoms, is in itself inadequate, and it will be shown directly that substances are known having such atoms and yet not being resolvable into enantiomorphs. Axes of the second order, it will be remembered (see page 602), are such that a rotation around them for their characteristic angle is always and inseparably accompanied by, and combined with, a reflection of the figure in its new position in the imaginary mirror, of which the plane is imagined to be perpendicular to the axis. By the movement of the figure around such an axis, and the reflection, it is always transformed into its image or inverted.

As an illustration Jaeger quotes the cases of two organic compounds possessing several asymmetric carbon atoms but neither a plane nor a centre of symmetry, and yet which are identical with their images on account of the possession of second order axes, and therefore are not resolvable into antipodes, but, on the contrary, are identical with their own images. The first is a derivative of tetramethyl-methane, in which two of the hydrogen atoms of each group are replaced by radicles X and Y in such a manner that the two upper groups CHXY are congruent, and at the same time are the non-superposable images of the two lower groups CHYX. Although this compound contains four asymmetric carbon atoms in its molecule, it is nevertheless identical with its image, because it possesses a tetragonal axis of the second order, although it has neither plane nor centre of symmetry. The other case is a derivative of tetramethylene, which likewise has neither plane nor centre of symmetry, but has a tetragonal axis of the second order perpendicular to the plane of the ring. It is therefore unresolvable, although it possesses no less than eight asymmetric carbon atoms.

Moreover, it would appear to have now been proved that it is possible to have a substance resolvable into optical isomers although no asymmetric carbon atom be present at all. Such a substance, for instance, is inosite,

[1] *Recueil des Trav. Chim. des Pays-Bas*, 1919, *38*, 171.

$C_6H_6(OH)_6$, described by Macquenne [1] and by Tanret,[2] the molecule of which possesses only axial symmetry, having a digonal axis of the first order. There are thus two possible arrangements of the atoms in the molecule, non-superposable images of each other, and therefore dextro and lævo optical antipodes are possible and have been isolated, although there are no asymmetric carbon atoms. Similar cases of very complicated organic compounds have also been described, and the two varieties separated, by Pope and Perkin,[3] and by Mills and Bain.[4]

It has to be remembered that the exhibition of optical activity in solution is a much simpler phenomenon than its display in the crystals. The structure of the latter depends on many other influences besides molecular structure, whereas the exhibition of optical activity in solution is directly due to the molecules themselves. Hence many cases of the latter occur, while the crystals of the same substances show no sign of enantiomorphism and optical activity, and these cases include some in which the molecules possess no asymmetric carbon atoms but exhibit optical activity in two antipodes by virtue of their being non-superposable with their images.

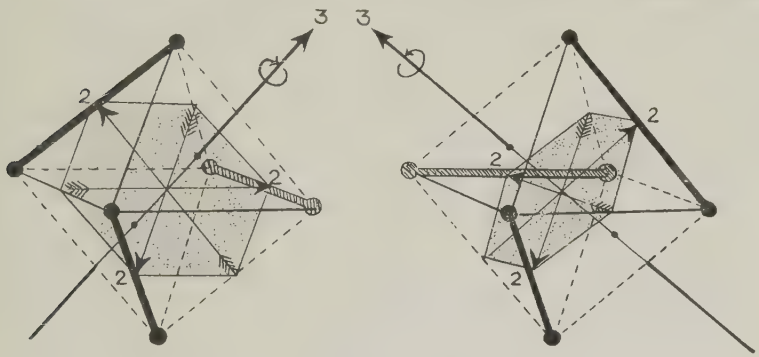
Some remarkable cases of optical activity, however, in both crystals and solution, have recently been brought to light by Werner,[5] in the course of the development of his "co-ordination" method of regarding chemical constitution, and by Jaeger,[6] who has followed the subject up with great industry. The substances, moreover, are of an entirely new type. In his researches on the complex compounds of trivalent metals Werner found that the salts with complex "ions" of the type $\{M . X_3''\}$, in which M is a trivalent metal and X is a dibasic acid radicle or a molecular residue of a strong divalent pseudo-base, could be separated into two optical antipodes. The essence of the case is that we have three identical radicles grouped in space around a trivalent metallic atom, in such a manner that the configuration of the molecule is not superposably identical with its own mirror-image. That is, configuration of the molecule is here alone concerned, no asymmetry of any elementary atom, in the sense understood by Van 't Hoff and Le Bel, entering at all into the matter. Indeed, the atoms of the metals in question, chromium, cobalt, iridium, and rhodium, possess a relatively highly symmetrical structure, as we know from the results of recent researches on atomic structure, there being nothing indicative of asymmetry so marked as to be capable of producing the extraordinary optical properties in two complementary varieties observed in their derivatives; and it is solely because of the absence of any second order symmetry element that these compounds differ from their images, just as in the case of the inosites. They may strictly be called "dissymmetrical molecules."

Instead of the six ammonium radicles which are present in the complicated ammonium compounds of these metals, chromium, cobalt, iridium, and rhodium, with which Werner had been working, it was found possible

[1] *Ann. Chim. Phys.*, 1893, *29*, 271.
[2] *Compt. rend.*, 1899, *109*, 908.
[3] *Journ. Chem. Soc.*, 1910, *99*, 1510.
[4] *Ibid.*, 1910, *97*, 1866.
[5] *Ber. der Deutsch. Chem. Ges.*, 1909, *42*, 981.
[6] *The Principles of Symmetry* (Amsterdam), 1917, and *loc. cit.*

to substitute three molecular groups of a divalent pseudo-base such as ethylene diamine, $C_2H_4(NH_2)_2$ or $H_2N.CH_2.CH_2.NH_2$, which for short may be written "Eine." Or we may substitute for the six radicles of a monobasic acid, in the salt formed by any one of these metals with the acid, three radicles of a dibasic acid such as oxalic, COOH . COOH, or malonic, $COOH.CH_2.COOH$. The new ionic compound of metal and base or acid radicle is then found capable of combining with the halogen radicle of a halogen acid, or the acid radicle of nitric, sulphocyanic, perchloric, or sulphuric acid; and also it may function as an "ion" of opposite character and combine with the strongly basic alkali metal potassium. The result is the formation of a series of compounds of which two, say of the metal rhodium, may serve as the type, namely, $Rh(Eine)_3R_3$ and $Rh(C_2O_4)_3K_3$. A space model represented in Fig. 876 will exhibit the antipodic nature of the two varieties possible most clearly.

It is supposed to represent a central atom of the trivalent metal,



Dextro. Lævo

FIG. 876.—The Symmetry of the Ions $[MX_3'']$

surrounded by the six places of ordinary co-ordination, represented in space by the corners of a regular octahedron of which the atom forms the centre. The configuration obviously exhibits the symmetry of quartz, there being a bipolar trigonal axis and three digonal axes in a plane perpendicular thereto, no other symmetry elements being present than these axes of simple rotation. The atomic complex is consequently non-superposable with its image and the two varieties are truly different enantiomorphs. No question of the asymmetry of any atom, metallic or other, enters into the case.

Jaeger has investigated a large number of salts of this type, such as $Co(Eine)_3Br_3$, $Rh(Eine)_3I_3$, $Ir(C_2O_4'')_3K_3$, $Rh(C_3H_2O_4)_3K_3$, and $Co(Eine)_3(NO_3)_3$; also some of mixed type, such as $Cr(C_2O_4)(Eine)_2Br$.

In many of the cases the fission of the two optical antipodes has succeeded perfectly, both as regards the solutions and the enantiomorphous crystals. In others, although there is ample evidence of crystallographic enantiomorphism from the physical properties, the two varieties of crystals have not been definitely geometrically demonstrable, owing to the faces

exhibited having only been the holohedral ones common to both the enantiomorphous and holohedral classes of symmetry of the system developed, a very common difficulty, and which may at any moment be overcome by finding the essential lower-class faces developed on a new crop of crystals. So many cases have been found of such faces on certain of the salts that there can be no doubt whatever as to the truth of the principle they support.

The salts of the type $Co(Eine)_3R_3$ are reddish-brown, the corresponding ones of rhodium are colourless, and those of chromium orange; $Co(C_2O_4)_3K_3$ is emerald green in colour, while the corresponding compound of iridium is orange.

The degree of optical activity surpasses that of all hitherto known organic substances, in solution, amounting in one case to ten times the rotation of cane sugar. Moreover, the dispersion of the rotation for different wave-lengths of light is so great that most curious phenomena, very difficult to unravel, are presented.

All of these substances form racemic molecular compounds of the two enantiomorphous varieties, and it has been by the resolution of these racemic substances that the two optical antipodes have in most cases been isolated. The forms of the racemic compounds are, as usual, totally different, and often contain water of crystallisation. Many of the optical antipodes also contain water of crystallisation, but it is different in amount to that contained by the racemic substance.

The molecular rotation M_D for sodium light of a few of these substances may now be given. Under the same circumstances the rotation M_D of cane sugar is 280°, which will afford a good means of comparison of the optical activity of these extraordinary substances with ordinary rotations.

		M_D.
Cobalti-oxalo-diethylene-diamine bromide . .	$\left\{Co\begin{matrix}(C_2O_4)\\(Eine)_2\end{matrix}\right\}Br$	2525°
Chromi-oxalo-diethylene-diamine bromide . .	$\left\{Cr\begin{matrix}(C_2O_4)\\(Eine)_2\end{matrix}\right\}Br$	1100
Cobalti-triethylene-diamine iodide . . .	$\{Co(Eine)_3\}I_3$	1072
Cobalti-triethylene-diamine thiocyanate . .	$\{Co(Eine)_3\}(SCN)_3$	781
Chromi-triethylene-diamine iodide . . .	$\{Cr(Eine)_3\}I_3$	378
Rhodi-triethylene-diamine iodide . . .	$\{Rh(Eine)_3\}I_3$	329

But the most remarkable salt of all, the subject of the latest memoir of Jaeger,[1] is the racemic cobalti-trioxalate of potassium, $K_3\{Co(C_2O_4)_3\}.3\frac{1}{2}H_2O$, belonging to a series previously described of racemic salts of chromium, rhodium, and iridium. The series is not an isomorphous one, as the amounts of water of crystallisation contained in the different members differ. But they are each and all separable by spontaneous fission into two enantiomorphous varieties, the crystal system and class of which pair are different from those of the racemic compound itself, as is usual.

Potassium cobalti-trioxalate is prepared by heating on a water-bath

[1] *Kon. Akad. van Wetensch.*, Amsterdam, 1918, *21*, No. 5.

with continuous stirring a mixture of 25 grammes cobalt carbonate, 250 grammes of a saturated solution of potassium oxalate, and 230 c.c. of a saturated solution of oxalic acid. After cooling to 40° C. 30 grammes of peroxide of lead PbO_2, and a little later 50 c.c. of a 50 *per cent.* solution of acetic acid are added. The filtered liquid is precipitated with alcohol, and the green precipitate of potassium cobalti-trioxalate separated and washed with alcohol. All these operations require to be carried out in a dark room, as the substance is rapidly attacked by light. The salt is next purified by converting it into the strychnine salt, by adding strychnine sulphate to a solution of the salt, and subsequently decomposing the strychnine salt with potassium iodide; the filtrate from the strychnine iodide yields, on precipitation with alcohol, a very pure preparation of racemic potassium cobalti-trioxalate, $K_3\{Co(C_2O_4)_3\} . 3\frac{1}{2}H_2O$.

Saturated solutions of this pure precipitate, when evaporated in the dark at a temperature only just above 0° C., deposit good crystals of this racemic salt with $3\frac{1}{2}H_2O$, of triclinic symmetry. At ordinary summer temperature, however, about 18°, in a dark room, quite different dark green trigonal crystals are deposited containing one molecule of water, $K_3\{Co(C_2O_4)_3\} . H_2O$, consisting of a mixture of the two optical antipodes; some of the individual crystals are of the dextro variety and others of the lævo-gyratory form. In general appearance they are alike, however, as only holohedral facial-forms are usually developed, the hemihedral facets of the right or left trapezohedron or right or left trigonal pyramid being less commonly developed, although they were clearly present on a few of the measured specimens. The temperature of transition of the racemic compound into the enantiomorphous pair of antipodes was determined exactly, and found to be 13·2° C. Below this temperature the solubility of the inactive racemic form with $3\frac{1}{2}H_2O$ is less than that of the two antipodes, whereas above 13·2° it is greater.

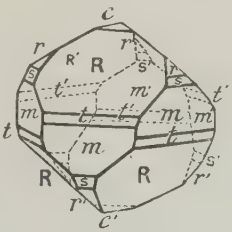


FIG. 877.—Dextro.

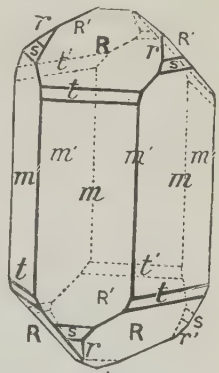


FIG. 878.—Lævo.

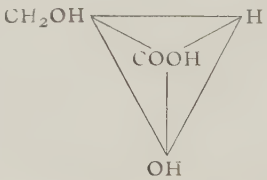
The Dextro and Lævo Crystals of Potassium Cobalti-trioxalate.

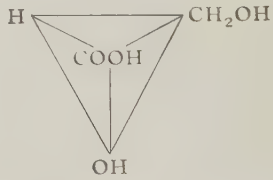
Two typical crystals of the dextro and lævo-gyratory forms are represented in Figs. 877 and 878.

They belong to the trigonal trapezohedral class 18. The Bravais-Miller axial ratio $a:c=1:0{\cdot}8968$; the Millerian rhombohedral axial angle $\alpha=100°\ 27'$. The forms shown are $R=\{10\bar{1}1\}=\{100\}$, which is large and predominant in right-hand crystals; $c=\{0001\}=\{111\}$ small; $m=\{1010\}=\{2\bar{1}\bar{1}1\}$ predominant in left-hand crystals; $r=\{01\bar{1}1\}=\{22\bar{1}\}$; $s=\{02\bar{2}1\}=\{11\bar{1}\}$; $t=\{20\bar{2}1\}=\{5\bar{1}1\}$. The hemihedral form $x=\{22\bar{4}1\}=\{71\bar{5}\}$ was clearly observed and measured on a lævo-gyratory crystal.

The molecular rotation for yellow sodium light is no less than + 11,000°. Their density compared with water at 4° is 1·8893.

A typical Investigation of an Enantiomorphous Optically Active Substance.—A concrete example, taken from an actual original investigation by the author, may well conclude this chapter, as an indication of the mode of procedure when good crystals of a new substance are obtained, the solutions of which in solvents are optically active. It is the case of the crystals of the calcium salt of the dextro variety of glyceric acid, which were obtained by Frankland and Frew[1] in the year 1891 and measured by the author[2] in the same year. When the calcium salt of glyceric acid, CH_2OH is fermented by means of the *Bacillus ethaceticus* one half of the | acid in the salt only is destroyed, the remaining half (after iso- CHOH lation from the calcium salt by decomposition with oxalic acid) | being then found to be optically active, rotating the plane of COOH, polarisation to the right. Now glyceric acid has obviously one asymmetric carbon atom, that of the CHOH group, and if we imagine it as a tetrahedron with the four corners available for attachment each to a monovalent atom or group, it must be clear that there are two ways, each the mirror-image of the other, of representing the acid, namely, the following so far as is possible in one plane :





The molecule obviously also has neither symmetry plane, centre of symmetry, nor even a second order symmetry axis. It is therefore non-superposable with its image, and should form two optical antipodes.

The acid itself is viscous and apparently uncrystallisable, but its calcium salt, $Ca(C_3H_5O_4)_2 . 2H_2O$, was obtained in good crystals, which were investigated by the author. The acid may be obtained by careful decomposition with oxalic acid of the calcium glycerate (precipitation of the calcium as insoluble calcium oxalate occurring), after the fermentation of the salt as above described ; it is found to be dextro-rotatory as already mentioned, but the aqueous solution of the calcium salt is lævo-rotatory, to the extent of − 12·09 units of specific rotation for sodium light, or expressed (see page 1092) in the usual manner $[\alpha]_D = -12·09$. The sodium salt is also lævo-rotatory.

The results of the goniometrical measurements proved the crystals to be of monoclinic symmetry. A typical crystal is represented in Fig. 879, and its stereographic projection on the plane of symmetry in Fig. 880.

The crystal system is thus the same as that in which the dextro- and lævo-tartaric acids crystallise, and the goniometrical work very soon revealed the fact that the class was also the same, namely, the sphenoidal

[1] *Journ. Chem. Soc.*, 1891, *59*, 96. [2] *Ibid.*, 1891, *59*, 233.

or monoclinic-hemimorphic class 4. For while four of the forms developed, $a=\{100\}$, $c=\{001\}$, $r'=\{\bar{2}01\}$, and $p=\{110\}$, were the same as would be present on a holohedral crystal, and were all represented by their full number of faces, yet one of them, p, consisting of four faces (110), ($\bar{1}10$), (1$\bar{1}$0), and ($\bar{1}\bar{1}$0), exhibited a great difference of brilliancy, according as these faces were on the right or left of the crystal as seen in Fig. 879, the two first-mentioned faces (cutting the right half of the digonal symmetry axis b) being bright, while the two last-mentioned faces (cutting the left-hand half of the symmetry axis) were dull. Further, two of the other four forms, $o=\{111\}$ and $m=\{011\}$, were only found on the right, and the remaining two forms, $s=\{\bar{1}\bar{1}1\}$ and $n=\{\bar{2}\bar{1}1\}$, were only present on the left-hand side of the crystal and of the digonal axis b. The faces of the left distinguishing forms s and n were also dull, while the right-hand distinguishing forms m and o were represented by brilliant faces affording excellent reflections of the goniometer signal. The crystal elements and table of angles are given on the following page:

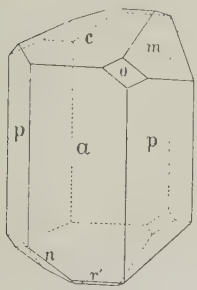


FIG. 879.

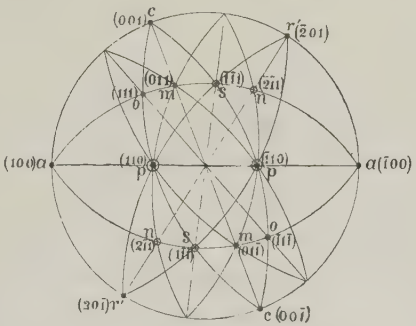


FIG. 880.

A Crystal of Calcium Dextro-glycerate and its Stereographic Projection.

The cleavage direction was common to both varieties, being paralle to the basal plane $c=\{001\}$. The optical properties confirm the monoclinic nature of the symmetry, but are not such as enable the class to be distinguished. The optic axial plane is the possible (but not active) symmetry plane $b=\{010\}$, which is not developed as a facial plane. The first median line is nearly normal to (2° from) the basal plane, making an angle of 23° with the vertical axis c (the basal plane being inclined 20° 54′ thereto). A crystal which is tabular parallel to the basal plane, or a cleavage plate, consequently shows the interference rings and brushes well. A section-plate truly cut perpendicularly to the first median line gave for the apparent angle in air 2E the values 51° 35′ for lithium light, 52° 30′ for sodium light, and 53° 50′ for thallium light; and for the true optic axial angle $2V_a$ for the same three wave-lengths (by combination with the results for a plate perpendicular to the second median line) 34° 56′, 35° 28′, and 36° 16′. The double refraction was positive, and the values of the intermediate refractive index β for the three wave-lengths just mentioned were 1·4496, 1·4521, and 1·4545.

The crystals have not yet been investigated for their optical rotation, as crystal individuals of considerable size are necessary, especially for the difficult cases of symmetry so low as monoclinic. The author hopes some day to be in the position of being able to procure such large crystals,

Crystal system: monoclinic, class 4, sphenoidal or monoclinic-hemimorphic. Habit: prismatic. Axial angle: $\beta = 110° 54'$.
Ratio of axes: $a : b : c = 1{\cdot}4469 : 1 : 0{\cdot}6694$.
Forms observed: $a = \{100\}$; $c = \{001\}$; $r' = \{201\}$; $p = \{110\}$; $m = \{011\}$; $o = \{111\}$; $s = \{1\bar{1}1\}$; $n = \{2\bar{1}1\}$.

Angle measured.	No. of Measurements.	Limits.	Mean observed.	Calculated.
$ap = 100 : 110$	42	52° 32′ — 54° 16′	53° 29′	*
$pp = 110 : \bar{1}10$	20	72 7 — 73 33	73 4	73° 2′
$ac = 100 : 001$	13	68 22 — 69 42	69 3	69 6
$cr' = 001 : \bar{2}01$	13	52 4 — 52 31	52 13	*
$r'a = 201 : \bar{1}00$	13	58 35 — 58 46	58 41	*
$cm = 001 : 011$	10	31 47 — 32 19	32 3	32 2
$r'n = \bar{2}01 : 2\bar{1}1$	2	29 43 — 29 48	29 45	29 47
$ao = 100 : 111$	7	53 59 — 54 10	54 3	53 54
$om = 111 : 011$	7	18 20 — 18 35	18 26	18 29
$ma = 011 : \bar{1}00$	13	107 22 —108 24	107 41	107 37
$an = \bar{1}00 : 2\bar{1}1$	11	62 32 — 63 44	63 6	63 10
$ns = 2\bar{1}1 : \bar{1}\bar{1}1$	1	—	21 35	21 27
$sa = \bar{1}\bar{1}1 : 100$	3	94 49 — 95 34	95 18	95 23
$po = 110 : 111$	9	43 51 — 44 44	44 35	44 38
$oc = 111 : 001$	9	32 56 — 33 15	33 7	33 7
$cs = 001 : \bar{1}\bar{1}1$	7	41 32 — 43 2	42 10	42 17
$sp = \bar{1}\bar{1}1 : \bar{1}\bar{1}0$	7	59 15 — 60 54	59 59	59 58
$pc = \bar{1}\bar{1}0 : 00\bar{1}$	14	77 2 — 78 21	77 42	77 45
$cp = 00\bar{1} : 110$	16	101 39 —103 36	102 16	102 15
$pm = 110 : 011$	9	52 15 — 53 25	52 42	52 41
$mn = 011 : \bar{2}\bar{1}1$	5	79 5 — 79 26	79 15	79 12
$np = 2\bar{1}1 : \bar{1}\bar{1}0$	5	47 41 — 48 23	48 4	48 7
$pr' = 110 : \bar{2}01$	14	106 35 —108 42	108 5	108 1
$r'p = \bar{2}01 : \bar{1}\bar{1}0$	26	70 54 — 73 32	71 55	71 59
$ps = \bar{1}\bar{1}0 : 1\bar{1}\bar{1}$	5	66 42 — 67 17	67 4	67 5
$sr' = 1\bar{1}\bar{1} : 20\bar{1}$	6	40 36 — 41 29	41 5	40 56
$pm = \bar{1}10 : 011$	3	75 5 — 76 21	75 37	75 45

and as perfectly clear, as Dufet was eventually able to obtain in the case of tartaric acid. In any case, to have worked through the goniometry and ordinary optical properties of a new enantiomorphous substance will have elucidated the method of procedure with such substances in the most practical manner possible.

CHAPTER LVI

THE THERMAL PROPERTIES OF CRYSTALS

Heat Radiation through Crystals.—The long waves of heat in the ethereal medium behave precisely similarly to the shorter ones of light radiation, crystals transmitting them in a manner entirely governed by their symmetry, and thus being as regards heat likewise either isotropic, uniaxial, or biaxial. Transparency to light waves, however, is not exactly paralleled in the same crystal substance by transparency to heat waves, or **diathermancy,** as it is called; and the diathermancy may be different for heat waves of different wave-length, the degree of absorption varying with the wave-length. Only a very few crystalline substances are practically perfectly diathermanous for heat waves of all lengths, prominent amongst them being rock-salt NaCl, sylvine KCl, and the corresponding bromides and iodides of sodium and potassium, silver chloride AgCl, and zinc blende ZnS. All these are isotropic, cubic, substances. A remarkable case in the opposite sense, of a substance perfectly transparent to light waves (which remain white and uncoloured), yet which is very absorbent of heat rays, and in various degrees according to their wave-length, is potash alum $KAl(SO_4)_2 . 12H_2O$.

Melloni, who investigated this subject of the transmission of radiant heat waves through solid and liquid substances, found that rock-salt transmitted 92 *per cent.* of the rays, while alum only transmitted 12 *per cent.* A solution of alum in water transmitted also 12 *per cent.*, and pure distilled water only 11 *per cent.* of the heat radiation. A rock-salt train of lenses and prisms is therefore a most valuable spectroscopic equipment for experiments on radiant heat. (As sodium chloride is hygroscopic, it must be kept in a dry place.) And a solution of alum, or pure water itself, forms an excellent screen (in a suitable cell) for removing the heat waves which accompany those of light, when the latter only are being studied and the former would prove deleterious. For this latter reason a cell of water or alum solution is always interposed between the lantern and the large polarising calcite Nicol prism of the projection polariscope, to absorb the heat rays from the electric arc (see Fig. 636 and its description, pages 857 and 858).

The waves of heat are subject to the same law of reflection (the angle of reflection is equal to the angle of incidence) at the surface of a crystal as light waves, and part of the heat ray is reflected in accordance with

this law and part is transmitted (refracted). The reflected and refracted parts suffer more or less of plane polarisation, dependent on the angle of incidence, as occurs with light waves. In the case of an optically isotropic, cubic, substance no double refraction for heat waves occurs, and the transmission takes place with equal velocity in all directions, but with different velocity for heat rays of different wave-lengths, a 60°-prism thus producing a heat spectrum, just as it does the light spectrum, the heat spectrum and the infra-red overlapping. The single refractive index for heat waves is thus different for heat waves of different wave-lengths.

In uniaxial crystals (trigonal, tetragonal, or hexagonal) the heat rays are doubly refracted in all directions except that of the optic axis, which is thus also a singular axis for radiant heat; and the two rays are rectangularly polarised with respect to each other. The fact was first

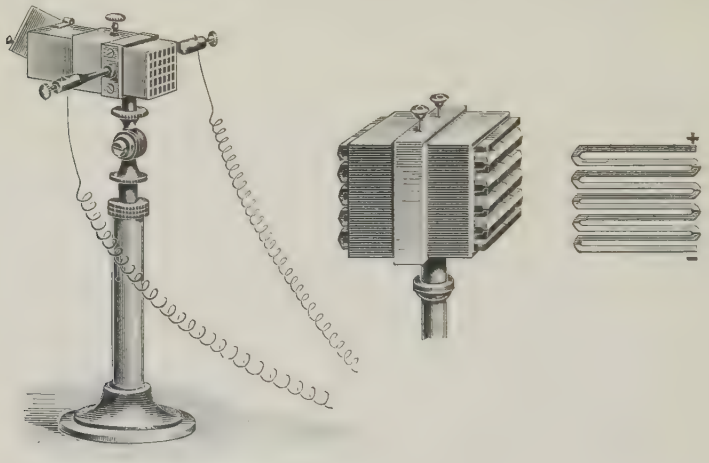


FIG. 881.—The Thermopile.

fully proved by an investigation of Knoblauch with calcite. Quartz rotates the plane of polarisation of heat waves, just as it does that of light waves, and it has been proved that for the dark heat waves of the infra-red radiation through quartz the amount of rotation of the plane of their polarisation diminishes with their refractive power, and becomes almost *nil* for a wave-length as far removed from the extreme red of the spectrum as is violet light from the latter.

In biaxial crystals the double refraction occurs in a manner analogous to that of light waves. If a mica plate, for instance, be examined on a rotating stage between crossed Nicols, it is found to become impervious to the heat rays four times, namely, when its axial directions are at the 0°, 90°, 180°, and 270° positions, during a complete rotation; while at the intermediate four positions, when the axial directions are 45° from each of the positions just quoted, it exhibits the maximum diathermancy.

For the measurement of radiant heat transmitted through crystals a

more or less refined method is necessary. The principle of all such instruments is that a surface coated with lamp-black or platinum-black absorbs such a large proportion of the rays of radiant heat projected on it, and becomes thereby so regularly raised in temperature, that the measurement of its rise of temperature affords an excellent relative measure of the energy of such radiation.

A thermopile is generally employed for the purpose, the elements of which are usually the two metals antimony and bismuth, the former of which occupies the one extreme end and the latter the other end of the thermo-electric list of elements referred to in the section on Thermo-

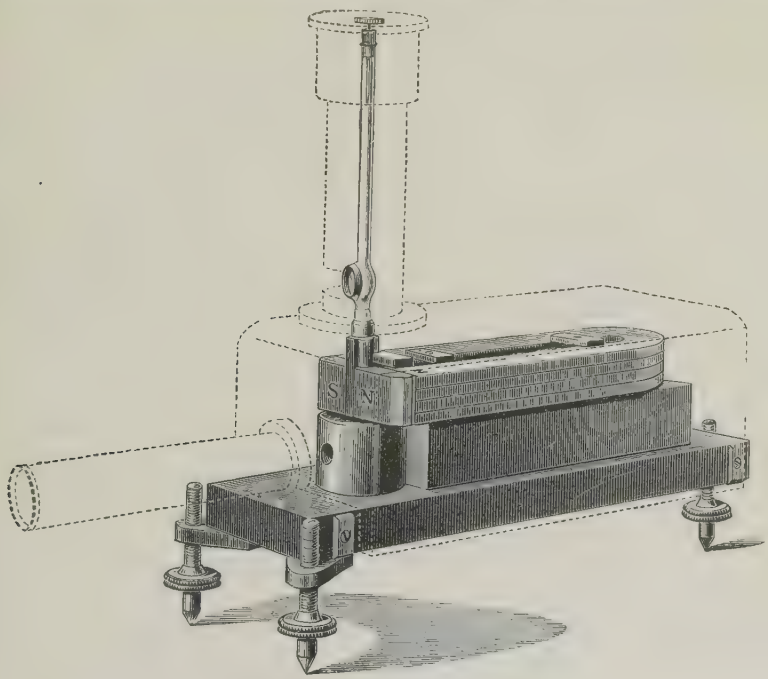


FIG. 882.—The Radiomicrometer.

electricity in Chapter LIX. The junctions of the several couples forming the pile are coated with lamp-black or platinum-black, while the single alternating elementary bars are separated by mica or other insulating material. The junctions are arranged at the ends of the bars, and are brought very close together, so that the whole combined end forms a flat surface of small area which can be coated with the black and arranged to lie at the apex of a receiving cone. Fig. 881, which shows two such thermopiles on the left and in the centre, differing slightly in the details of their construction but alike in principle, will render the arrangement clear, except that the conical receiver at each end is omitted. The mode of arranging and attaching the alternate bars of antimony and bismuth is shown separately on the right. On presenting one of the two cones towards

the oncoming radiations, the latter become absorbed and the junctions heated, the temperature being indicated by the calibrated galvanometer arranged in the circuit with the thermopile.

A more delicate instrument is the radio-micrometer of Prof. Boys, shown in Fig. 882, and the essential parts in section in Fig. 883. In this instrument the thermopile and galvanometer are combined, and being very small swing as a needle, the suspension being by a quartz fibre. The thermopile portion consists of a miniature antimony-bismuth couple, consisting of two minute bars of the metals soldered to the edge of a blackened copper plate 2 mm. square, the other ends of the bars being connected by a light copper loop directly suspended by the quartz fibre between the poles of a powerful permanent magnet. The deflection of the miniature suspended circuit is measured by the movement of a beam of light reflected from a small attached mirror.

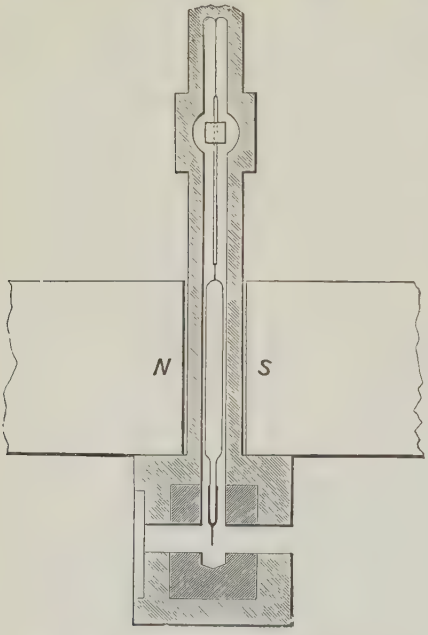


FIG. 883.—Radiomicrometer, the Suspension.

When heat radiation falls on the blackened face of the little copper plate the lower junction of the antimony-bismuth couple becomes heated, and a current traverses the circuit. As this is freely suspended in a strong magnetic field it is deflected, on the same principle as the moving coil galvanometer. It thus acts as an ideal thermopile without the need for a separate galvanometer. The reflecting miniature mirror is attached to the upper part of a capillary glass tube which forms the intermediary between the quartz fibre above and the copper wire circuit below. The radiation falls upon the thermo-junction through a transverse aperture, closed at the far end by a glass plate for inspection purposes; this aperture is drilled out of a mass of soft iron (shaded dark in Fig. 883) surrounding the couple, which serves to prevent disturbance due to diamagnetism. The dotted lines in Fig. 882 indicate a protective cover of thick wood for the whole instrument, a paper tube being attached to it in front of the radiation aperture for the more convenient admission of the radiation.

Another refined instrument is the bolometer of Langley, in which a thin strip of blackened metal forms one of the arms of a Wheatstone bridge, and the rise in its temperature is measured by the increase in the resistance of the metal. It is shown in section in Fig. 884 It was first constructed

in the year 1881 [1] for the study of the distribution of heat in the solar spectrum. The essential feature is a grating or parallel system of elements in the form of strips about a centimetre long, half a millimetre wide, and 1/100 to 1/500 mm. thick, punched from a single thin sheet of platinum or palladium, or even steel, foil, the ends or junctions of the strips being thus part of the same piece of metal as the rest of the grating. This is placed in one of the arms of the Wheatstone bridge, and a duplicate grating screened from radiation counterbalances it on the other arm with the aid of a variable resistance, so that an exact counterpoise can be attained in the galvanometer circuit. A couple of Daniell's cells supply the necessary current, which divides itself between the two arms. When heat radiation

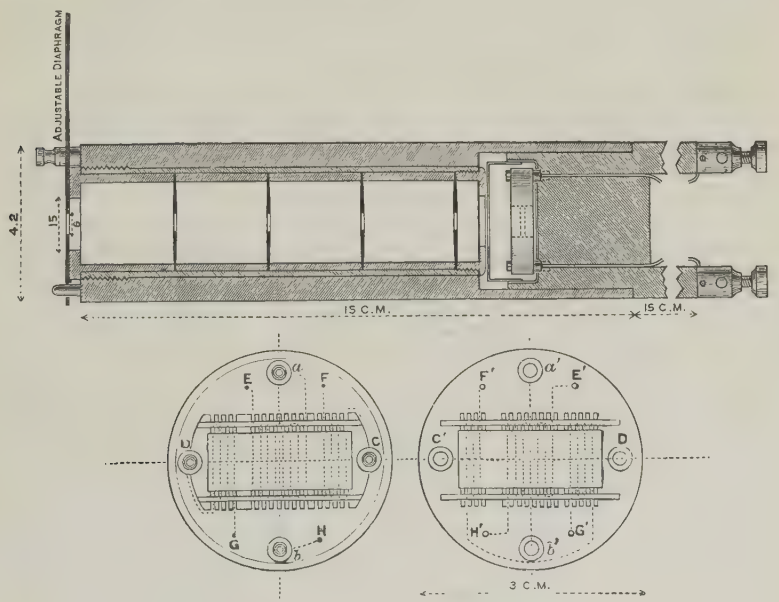


FIG. 884.—Langley's Bolometer.

falls on the exposed grating the resistance is increased and the current thereby weakened in that arm, so that the galvanometer needle is deflected, and the amount of the variable resistance required to be inserted to bring it back to zero is observed. Change of temperature no greater than the 1/10,000th of a degree centigrade can be detected, and owing to the thinness of the strips the action is practically instantaneous. The whole is enclosed in a copper-lined chamber, which is itself enclosed in a much longer ebonite cylinder, provided with four diaphragms pierced by central apertures of 6 mm. diameter, arranged at equal intervals formed by short ebonite separating inner cylinders; this arrangement of diaphragms proves an effective device against disturbing air currents. The admission aperture may be varied in size, a whole series of circular openings of

[1] *Proc. Amer. Acad. of Arts and Sciences*, 1881, *16*, 342.

different sizes being provided on a rotating circular disc attachment. After the fourth diaphragm comes the grating, then a solid layer of non-conducting material through which the connecting wires are led to the binding screws. The short space behind this serves for the reception of the compensating grating and variable resistance. Steel, platinum, or palladium are suitable for grating material on account of their high electrical resistance, and the considerable alteration of their resistance with change of temperature, as well as on account of their tenacity, ductility, and resistance to oxidation.

The main results of Melloni with crystals are given in the following diathermancy table, the numbers representing percentages of the incident heat radiation transmitted by the crystal, the source of heat being an incandescent platinum spiral, and the receiving instrument a delicate thermopile.

DIATHERMANCY OF CRYSTALS.

Rock-salt, NaCl	92	Barytes, $BaSO_4$	18
Fluorspar, CaF_2	69	Gypsum, $CaSO_4 . 2H_2O$	5
Iceland spar, $CaCO_3$	28	Alum, $KAl(SO_4)_2 . 12H_2O$	2
Quartz, SiO_2	28	Pure ice	0
Potassium bichromate, $K_2Cr_2O_7$	28		

Conduction of Heat.—The phenomena of heat conduction by crystals (as distinguished from the transmission through them of ethereal radiant heat waves) have been rendered readily demonstrable by the well-known method first described by M. de Senarmont [1] in the year 1847. The method consists in laying on the surface of a plate of the crystal, or on the face of a tabular crystal of the substance to be investigated, a very small piece of wax and warming both crystal and wax slowly to the temperature of the melting point of the latter, when it spreads itself in a thin layer over the entire face, any excess being allowed to run off by tilting the crystal. On cooling, the wax solidifies as a thin translucent film. It is then touched at a single point by a hot needle, or other metallic point, the heat being conveyed to the latter by conduction from the other end of the pointed metal rod or wire, at which other end furthest from the crystal the heat is applied, the crystals and its wax film being sheltered from the direct heat rays by suitable screening. Another mode of procedure is to drill a fine hole through the crystal plate and to lead through it a silver wire, or better, a fine silver tube, which can be heated in a similar manner from one end. This mode is illustrated in Fig. 885.

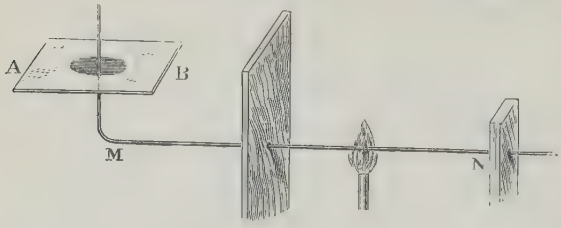


FIG. 885.—Method of M. de Senarmont.

As soon as the metallic point, wire, or tube adjacent to the crystal and wax feels the heat it begins to communicate it also to the crystal and wax.

[1] *Comptes rendus*, 1847, *25*, 459 and 707.

and the latter proceeds to melt around it in a patch the circumference of which is either a circle or an ellipse, according to the nature of the crystal plate; on cooling, the periphery of the melted zone is clearly marked by a little welt or raised ridge. If the crystal plate be such that conduction over its surface is equal in all directions, as would be the case with a cubic crystal or a plate of a uniaxial crystal cut perpendicularly to the axis, the figure is circular. If the crystal plate be that of a biaxial crystal, or of a uniaxial crystal cut otherwise than perpendicularly to the axis, the figure is an ellipse, the heat being conducted with different velocity in different directions in the crystal surface. For the directions of maximum and minimum conduction are always at right angles, just as are the vibration directions of the maximum and minimum light transmission. The major axis of the ellipse is the direction of greatest conductivity, and the minor axis that of the least conductivity in the crystal surface. The isothermal surfaces around the heated point of the crystal are in general a series of concentric ellipsoids, and the axes of these ellipsoids coincide with the axes of crystal symmetry, in the cases of those crystals which possess such axes (see page 1297).

When the plate is of considerable thickness, and is heated by a wire passing through a hole at right angles to the faces, the curves on the two faces are only true ellipses when the plate is parallel to a principal plane of the ellipsoid (parallel to a plane of symmetry or perpendicular to an axis of symmetry). In general, that is in other cases, the plate not being so symmetrically orientated, the curves will be egg-shaped ovals, with their broader ends oppositely situated to each other (turned in opposite directions), the plate being heated along a line and not at a single point. For when the source of heat is a line the curves on the two parallel faces of the plate are only similar ellipses when the line, that is the hole, is drilled in the direction of that diameter of the thermal ellipsoid which is conjugate to the direction of the plate faces. Or, otherwise expressed, the hole should be drilled in the direction conjugate to the faces with respect to the thermal ellipsoid.

Jannettaz[1] modified the method of de Senarmont by employing a small platinum ball to make the contact with the wax; a fine platinum wire was attached to it which could be heated by an electric current. The wire passed, just above the ball, through a flat dish containing water, to act as a screen to protect the wax from all heat rays passing by radiation towards the direction of the wax surface.

The best method of all, however, is one due to Röntgen.[2] The surface of the crystal plate, or the crystal face if a natural crystal of tabular form is being employed, is breathed upon and then immediately touched with the point of a heated wire. This disperses the film of moisture just around the spot touched. On then at once dusting with lycopodium powder the shape of the spot is clearly and more or less permanently revealed, as the powder adheres firmly to the remaining portion of the moisture film, while it readily falls off from the dry spot on shaking the crystal. The spot is

[1] *Ann. Chim. Phys.*, 1873 [4], *29*, 5.
[2] *Pogg. Ann.*, 1874, *151*, 603; also *Zeitschr. für Kryst.*, 1879, *3*, 17.

then seen to possess the circular or elliptical shape of the conductivity figure or "isotherm." The method gives excellent figures, capable of accurate measurement, thus facilitating the accurate determination of the relative lengths of the axes of thermal conductivity in the event of the figure being an ellipse.

A cleavage surface of stibnite, the naturally occurring sulphide of antimony, Sb_2S_3, which crystallises with orthorhombic symmetry and develops a perfect cleavage parallel to {010}, affords the means for an excellent demonstration of the production of an elliptical conductivity isotherm, either by de Senarmont's method (touching the wax film in this case with the point of a heated wire), or by Röntgen's method. The ellipse is found in either case to have its major axis parallel to the vertical crystal axis *c*, and its minor axis parallel to the horizontal axis *a*, heat being conducted in stibnite more readily along the direction of the vertical axis *c* than along the brachy-diagonal axis *a*. According to H. L. Bowman a thin layer of ammonium chloride, obtained by sublimation, answers well as a substitute for de Senarmont's wax coating. The application of a heated point volatilises the salt, and leaves the surface of the stibnite crystal (cleavage plate) exposed. The resulting figures are clearly visible, but the specimens must of course be subsequently protected from injury in a glass tube or otherwise.

A cleavage plate of gypsum, selenite, $CaSO_4 . 2H_2O$, the well-known monoclinic mineral which cleaves so readily parallel to the symmetry plane {010}, may also be used to demonstrate very clearly the conductivity isotherm. In this case the major and minor axes of the elliptical figure produced are oblique to the crystal axes and to the edges of the crystal plate, while at right angles to each other, as illustrated in Fig. 886; for the monoclinic symmetry does not fix the positions of the isothermal axes, which may lie anywhere in the plane of symmetry consistent with their mutual rectangularity.

In the year 1898 H. L. Bowman[1] described not only the method to which reference has been made above in the case of stibnite, but also a simple, permanent, and effective method of producing curves of conductivity for heat on the faces of crystals containing water of crystallisation, gypsum and copper sulphate having been employed by him. A stout brass wire of $\frac{3}{16}$ inch diameter is filed at one end to a conical point. It is then supported in a vertical position with its point resting on the face of the crystal, and is heated by means of a Bunsen burner directed horizontally at a point 1 or 2 ins. above the end. The water of crystallisation is driven off by the heat, and an opaque white spot formed round the point. This spot has an elliptic outline, which approximates to the curve of conductivity.

If figures be produced on faces belonging to different forms, they can be seen to vary, in the directions and ratios of their axes, in accordance with the symmetry of the crystal. Fig. 886 shows the figures obtained on a typical crystal of gypsum. Figures may readily be obtained with a major axis of 5-6 mm. or more, but beyond this size the outline is rather apt to

[1] *Min. Mag.*, 1900, *12*, 353.

become irregular, the opacity extending outwards in streaks which, on the cleavage face, run nearly parallel with the edge [010 : 111].

No advantage appears to be gained by screening the crystal from the direct radiation from the source of heat.

Under the microscope the white patch is seen, near the margin, to consist of dots, which with a $\frac{1}{4}$ in. objective show a form resembling the "Verwitterungsflecken" described by Sohncke.[1]

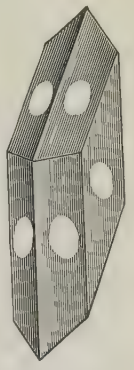


FIG. 886.—Curves of Conductivity on a Gypsum Crystal.

The thermal conductivity of some particularly large and well-formed crystals of bismuth have been determined by F. L. Perrot[2] by the method of de Senarmont, and also by a novel method, for the directions parallel to the crystallographic axis of the trigonal crystals and perpendicular thereto. In the first set, a pointed wire, heated by a Bunsen burner, was used to touch the surface of the metal covered with the easily fusible wax or other material. The major and minor axes of the elliptic form of the boundary of the melted material were carefully measured, and the square of their ratio gave the ratio of the conductivities. In the cases of four different crystals the ratios of the conductivity perpendicular to the axis to that parallel to the axis were found to be 1·288, 1·308, 1·408, and 1·390; the mean of the last three, by far the more perfect specimens, was taken as near the truth, namely, 1·368. Lownds[3] had previously found the same ratio for a single crystal of bismuth in his possession to be 1·42. Perrot then used in confirmation the second method, which is new. He placed a parallelepiped of bismuth on a heated iron surface, and then laid on its upper surface two crystals of substances fusing at known suitable temperatures. The time taken between the melting of these two small crystals was considered as being inversely proportional to the conductivity of the bismuth. The mean result of several experiments by this method for the ratio of the conductivities in bismuth perpendicular to and parallel to the axis, was again found to be 1·368. Cailler has pointed out on mathematical grounds that this method is not a safe one, but that in the case of the particular experiments of Perrot the error was probably not greater than 2 per cent. Hence, the ratio of the conductivities of bismuth may be taken as being very close to the number 1·37.

The conductivity for heat of the trigonal crystals (calcite class 21) of hæmatite, Fe_2O_3, has been determined by H. Bäckström,[4] using the methods of Röntgen and de Senarmont. Jannettaz had previously found the ratio of the conductivities to be 1·1, that along the principal axis being the smaller. By the Röntgen method, as the mean of six determinations Bäckström found the ratio to be 1·06. By the de Senarmont method the value afforded was 1·064. In order to be certain, however, he tried a third method. Two plates, respectively perpendicular and parallel to the axis,

[1] *Zeitschr. für Kryst.*, 1899, *30*, 1.
[2] *Arch. Sci. Phys. Nat.*, 1904, *18*, 445.
[3] *Phil. Mag.*, 1903, *5*, 152.
[4] Ofversigt af Kongl. Vetenskaps-Akad. Förhendlingar, Stockholm, 1888, *8*, 533.

were prepared and laid alternately between three copper plates carrying small thermo-elements, the five plates forming a small pile. In contact with the uppermost and the lowest (copper) plates were copper water baths maintained at different temperatures, and the temperatures between the upper and middle copper plate, and between the middle and lower copper plate, were determined by means of the thermo-couples fixed in the copper plates themselves. These temperature-differences were proportional to the resistance of the two hæmatite plates alternating with the copper plates; the resistance was due to the two factors, thickness of plate and its thermal conductivity. It was, therefore, readily possible to calculate the relative conductivities perpendicular to and parallel to the axis, and the ratio proved to be 1·11-1·12.

It is thus established that the thermal conductivity of crystals follows very similar laws to those governing their behaviour towards light. If the conductivity be supposed to start, as from a centre, from some point within the crystal, and to travel in a straight line, and its value along any radial direction from the central point be represented by the length of the straight line, the surface traced out by the terminations of all such possible straight lines radiating from this centre will be a sphere in the case of an isotropic crystal, an ellipsoid of revolution in the case of a uniaxial crystal, and an ellipsoid of general form with three unequal rectangular axes in the case of a biaxial crystal. In consequence, the shape of the isothermal curve in the surface of any crystal face or cut plate, which curve will be the locus of all positions which will have attained the same temperature, when the latter is being raised by conduction from a point in the surface, will be a circle when the experiment is performed on the face or cut (or ground) surface of a cubic crystal. The sphere (any one of a series of successive isothermal spheres) satisfies the equation $x^2 + y^2 + z^2 = r^2$, supposing the source of heat to be taken as the origin of the co-ordinates and r to be the radius. In the case of the thermal ellipsoid corresponding to any of the anisotropic systems of crystals, if A, B, C be the conductivities for heat along the axes of the ellipsoid, K the absolute conductivity of the substance, and the axes of reference be taken in the directions of the thermal axes of the crystal, then the ellipsoid satisfies the equation

$$\frac{x^2}{A} + \frac{y^2}{B} + \frac{z^2}{C} = \frac{r^2}{K}.$$

The axes of any one of the isothermal ellipsoids are directly proportional to the square roots of the three principal conductivities of the substance. (See Preston's "Heat" for a full mathematical discussion, pages 652–656.)

In the case of uniaxial crystals the thermal conductivity is either a maximum or a minimum in the direction of the optic axis, and the converse in all directions perpendicular thereto, the value varying between these two extremes according to the inclination of the radial direction under consideration to the axial direction. Uniaxial crystals may thus be thermally positive or negative, according as the spheroid is elongated or compressed along the axis. The isothermal curve is consequently only a circle for a plate or face perpendicular to the axis, that is, for the basal

plane ; for planes of all other situations it is an ellipse, and the relative lengths of the two axes of the latter differ most when the plate is parallel to the axis.

For biaxial crystals the thermal conductivity is different in all different directions, and the maximum and minimum values correspond to two directions at right angles to each other, which are thus the two extreme axes of the thermal ellipsoid ; perpendicular to the plane of these two rectangular axes is a third axis of the ellipsoid of intermediate value. The thermal conductivity in any other direction is afforded by the relative length of the radius of the ellipsoid parallel to that direction. In rhombic crystals the three axes are identical in direction with the three crystallographic axes a, b, c. In monoclinic crystals only one axial direction corresponds to a crystal axis, the unique axis of symmetry b. In triclinic crystals the thermal and crystallographic axes are in general all differently situated, but of course the three axes of the thermal ellipsoid are, as always, mutually rectangular, while the crystal axes, also as always for this crystal-system, are never rectangular.

These facts are of some practical value, besides in a very beautiful manner emphasising the parallel behaviour of crystals towards light and heat. For an investigation of the thermal conductivity curves by the methods of de Senarmont or Röntgen may be possible, and give valuable information, in the cases of crystals which are opaque to light, and thus serve the same purpose as an optical investigation, of confirming or even actually deciding the nature of the symmetry indicated only more or less clearly by the goniometrical investigation.

Measurement of Relative Conductivity for Heat in Solids obtainable in Quantity.—The relative conductivities of a number of solids, chiefly metals however, have been very accurately determined by Wiedemann and Franz, and there appears to be no reason why their method cannot be applied to crystals obtainable in considerable size, such as are many minerals. A bar of the substance is heated at one end, and its temperature at regular intervals along its length is taken by means of a sliding thermopile. It is a refinement of the well-known rough method of Despretz, in which thermometers are inserted at regular intervals in holes drilled in the bar. The bar was immersed, in the experiments of Wiedemann and Franz, in a glass chamber which could be rendered vacuous, and which in turn was immersed in a water bath provided with a thermostat, in order to maintain a constant temperature. The end of the bar was heated to 100° C. by a current of steam. The thermopile was graduated (calibrated) *in situ*, under similar conditions to those of the experiment, and special precautions were taken to ensure complete contact of the bar and the thermal junctions of the pile. A table of the results for metals is given on the following page, silver being taken as the standard of relative conductivity and valued at 100.

Experimental Determination of Absolute Conductivity for Heat of Crystals.—In order to arrive at a correct conception of heat conduction a plane lamina with parallel faces is best considered. If one face be maintained at the temperature θ_1, and the other at the different tempera-

RELATIVE CONDUCTIVITIES *in vacuo*.

Silver	100	Steel	10·3
Copper	74·8	Iron	10·1
Gold	54·8	Lead	7·9
Brass	24·5	Platinum	7·3
Tin	15·4	Bismuth	1·8

ture θ_2, there must be a persistent flow of heat through the substance of the plate from the hotter face to the colder one. Assuming the lamina to be homogeneous, the quantity of heat which flows through it has been experimentally proved to be proportional to the difference of temperature $\theta_1 \sim \theta_2$ of its faces. For laminæ of different thicknesses the flow will be inversely as the thickness e. The quantity of heat Q flowing will also be proportional to the area A of the lamina and to the time t. It will further depend on the material, that is, on the specific nature of the substance under investigation of which the lamina is composed, different materials having different powers of conducting heat, and this factor is usually represented by K. We then have

$$Q = K\frac{\theta_1 - \theta_2}{e}At.$$

If we suppose the lamina to be of unit thickness and area, and unit difference of temperature to occur between its two faces, the absolute conductivity K becomes numerically equal to the quantity of heat which flows through the lamina *per* unit of time. If we use the method of the differential calculus, and suppose the lamina to become infinitely small, represented by dx, and to exhibit an infinitely small temperature difference $d\theta$, we arrive at the conclusion that the quantity of heat flowing in infinitely small time will be

$$Q = -KA\frac{d\theta}{dx}dt.$$

When the steady state is established this reduces to

$$K\frac{d\theta}{dx} = \text{a constant}.$$

The quantity $\frac{d\theta}{dx}$ is the gradient of temperature, and the expression means that the flow of heat through unit area *per* unit time is equal to the absolute conductivity multiplied by the temperature gradient, and this has been experimentally proved to be a fact.

The determination of the absolute conductivity of solids can be carried out by three different methods, that of the Guard Ring, that of Forbes, and that of Ångström. The two latter methods are suitable for application to crystals, and have been so applied by C. H. Lees. A brief account will first be given of the three methods, and then a description of the work of Lees on the absolute conductivity of quartz and other crystalline substances.

The Guard Ring method is the obvious one of taking temperatures near the plane faces of the section-plate, across which the flow of heat is to be determined. But the practical difficulties are great when the plate is thin, as thermometers have to be

inserted in holes drilled vertically parallel to and very near each of the surfaces. Hence, only a comparatively very thick plate can be used for this method, really a block, and one of its surfaces forms the end of a chamber heated by steam, while the other face is the end of a similar chamber filled with ice. This method is clearly unsuitable for work with crystals. It is better adapted to use with liquids than solids, and it received its name from the circumstance that in using it to determine the absolute conductivity of mercury an outer vessel or "guard" of mercury was used to ward off radiation from or to the essential inner glass tube containing the mercury under investigation.

The method of Forbes involves two experiments, one statical, the determination of the temperature curve and temperature gradient at all points on a bar of the solid substance, and a dynamical one, the determination of the rate of cooling of the bar when uniformly heated and left to cool in air. In determining the conductivity of wrought iron two separate bars were used, of 8 feet length for the statical experiment, and only 20 inches for the dynamical one. The larger bar was heated at one end by being fixed in a crucible of molten lead or solder maintained at a constant temperature just above its melting-point. In order to determine the temperature curve ten thermometers were placed in holes drilled in the bar at regular intervals and filled up with mercury or fusible metal. The smaller bar had a single thermometer similarly arranged in the centre of the bar, and several others near it, and was heated uniformly by complete immersion in a cylindrical bath of heated fusible metal (4 parts lead, 3 of tin, and 3 of bismuth). It was then withdrawn and rested on two blunt-edged props to cool, the temperature being read off each minute during the cooling.

From the results of the statical experiment the temperature curve was plotted, and the value of $\frac{d\theta}{dx}$, the temperature gradient, was afforded for each point (section) of the bar. From the dynamical experiment the cooling curve was plotted, and from the combined results of both experiments a third curve was drawn, having rates of cooling for ordinates and corresponding lengths along the statical bar for abscissæ. This final curve was approximately logarithmic, so that the area between any two ordinates could be calculated, or measured with a planimeter. This area, for two very closely adjacent ordinates corresponding to the distance dx, is proportional to the quantity of heat radiated by this element of area per second. Hence, the area of the curve between the ordinate at the point x and the cold end of the bar represents the total loss of heat from the surface of the bar beyond the section, that is, the flow of heat across this section at the point x. The final result was to afford, in centimetre, minute, and centigrade degree units, the absolute conductivity K of wrought iron for temperatures from 0° to 200° C., the actual numerical value being calculated for every 25°. They were 12·36 at 0°, 11·80 at 25°, 11·15 at 50°, and so on, diminishing regularly down to 7·62 at 200° C.

Tait subsequently repeated and confirmed Forbes's experiments, and extended them to copper and lead. Callendar and Nicolson have since determined the conductivity of cast iron by Forbes's method, using a large bar, 4 feet in length and of 4 inches diameter, lagged like a steam-pipe to the depth of an inch in order to reduce surface loss of heat. It was heated by steam at one end, and cooled by a stream of water flowing through a calorimeter at the other. The heat transmitted was measured calorimetrically, and five thermometers were placed at intervals along the bar to determine the temperature gradient near the entrance to the calorimeter.

The method of Ångström consists of observations of the periodic

flow of heat in a bar, which is alternately heated and cooled at one end or some other definite part of its length, the centre being often chosen. Long bars were employed, 57 and 118 centimetres being the lengths of two employed in the chief determinations, the thicknesses being 25 and 35 millimetres, and the periodic heating and cooling was effected by enclosing the middle part of the bar in a chamber through which alternately steam and cold water could be circulated. When the alternation had been carried on for some time, the temperature at any part became steadily periodic, and the mean temperature constant. Thermometers were inserted in perforations at 5-centimetre intervals. With this apparatus Ångström found the value of K for iron and copper to be 9·77 and 54·62 respectively.

Callendar has also employed the method, using the same apparatus as he used for Forbes's method, by varying the steam pressure in the heater, so as to produce a simple harmonic oscillation of temperature, while the cool end was kept steady.

The **Method of Lees** [1] for the determination of the **Absolute Conductivity of Crystals** in different directions is an application of Forbes's method to the particular problem in hand, by causing the crystal to act as part of a metallic bar. The method was first suggested by Sir Oliver Lodge, and the form in which Lees carried it out was to prepare two absolutely similar bars of the same metal, and to place them end to end in the same straight line as a compound bar of double the length, and with the crystal section-plate gripped between them at their junction. Brass was used as the metal, and contact with the crystal plate was rendered the more assured by mercuric amalgamation of the gripping ends. The crystal lamina thus formed the central section of the whole compound bar, that is if we imagine it as infinitely thin it acted as a particular section, across which the flow of heat was to be measured. As it had appreciable thickness, however, the problem really resolved itself into determining the conductivity at those two infinitely thin sections formed by the two parallel surfaces of the crystal plate. The temperature curve along the bar was determined by means of thermo-electric couples of platinum-silver alloy and iron, immersed in miniature mercury cups drilled in the bar. The length of the compound bar was 67 cm, and its diameter 1·93 cm. The whole was packed in sawdust, and one end was heated by steam while the other end was immersed in cold water. From the temperature curve which was plotted the value of $\frac{d\theta}{dx}$, the temperature gradient, was obtained for each face of the crystal section-plate. The absolute conductivity K of the brass bars had previously been determined when placed end to end without any crystal between them, so that the value of K for the crystal could readily be calculated. The main results were the following:

For quartz parallel to the axis the absolute conductivity K was found to be 0·0299, and for any direction perpendicular to the axis 0·0158.

[1] *Phil. Trans.*, A, 1892, *183*, 481; *Mem. and Proc. Manchester Phil. and Lit. Soc.*, 1890-91, *4*, 17.

The conductivity of this uniaxial mineral is thus twice as great along the axial direction as it is transversely thereto, and this larger axial value is the highest conductivity observed among the crystalline substances investigated by Lees. It is, of course, much less than that of the brass of which the bars were constructed, which was 0·27, nine times as much as that of quartz. For Iceland spar along the axis the value 0·0100 was obtained, and for the direction perpendicular to the axis 0·0084.

For mica perpendicular to the cleavage the very low value 0·0018 was afforded. Rock salt for any direction (the crystals being cubic, isotropic) gave 0·0138. These results all refer to the thermal conductivity between the temperatures 25° and 35° C., and are expressed in C.G.S. units. As affording a valuable comparison with a transparent non-crystalline solid, it may be mentioned that the values similarly obtained for crown and flint glass were respectively 0·0024 and 0·0020, values only slightly greater than for mica. It will thus be seen that the average thermal conductivity of quartz is more than ten times as much as that of glass. It is to this property of relatively high conductivity that quartz owes its long-known extraordinary coldness to the touch. Spheres of rock-crystal were much valued by the ancient Romans in the days of Imperial Rome for their refreshing coolness when held in the hand during the heat of midsummer. This is clearly referred to in the two following quotations from Propertius:

> Oh what avails the purple's Tyrian glare,
> Or that my hands the limpid crystal bear?

> Now courts the breeze with plumes of peacocks fanned,
> Now holds the flinty ball to cool her hand.

Lees concluded from his results that for these transparent crystalline substances no such comparison between their thermal conductivity and velocity of propagation of light can be made, as has been made by Kundt for metals. The thermal conductivities vary enormously compared with the very small change of refractive index for light. He also remarks that it is singular that quartz and rock salt, which are diathermanous bodies, should also be good conductors, quartz being a better conductor than bismuth (0·017 according to Lorenz). He further expressed the opinion, since so remarkably verified, that fused quartz, on account of its high conductivity, would prove very suitable for vessels subject to sudden change of temperature, and for delicate thermometers.

The Thermal Expansion of Crystals.—The thermal expansion of a solid body is expressed by its "linear coefficient of expansion," which is symbolised by α, and is the amount of extension of the body which unit length of it undergoes in the direction of that length on raising the temperature of the body through one degree centigrade. The expression is not itself a constant, but consists of two constants a and b of which twice the latter is multiplied by the number of degrees of temperature. That is, the linear coefficient of expansion α for any temperature t is:

$$\alpha = a + 2bt.$$

The coefficient thus varies regularly with the temperature, the increment

per degree of the latter being $2b$. Thus, for example, the coefficient is not the same for 50°-51° or 100°-101° as it is for 0°-1°, but as a rule considerably different and greater in each case; occasionally it happens, however, that the value $2b$ is a decrement, the sign of $2b$ being negative. It is regular at any rate, so long as the chemical composition of the substance remains unchanged, and if the body be crystalline, for the same direction in the crystal; also, in the cases of polymorphous substances, so long as the symmetry remains the same, that is, so long as the particular crystalline modification persists. The expression for α above given is also the mean linear coefficient between any two temperatures of which the mean is t. The mean coefficient between 0° and $t°$ is $a+bt$.

The above expression for α is derived from the following considerations. If the length of the solid substance at 0° be represented by L_o, and the length at $t°$ by L_t, the nature of the change of length is adequately represented by the formula

$$L_t = L_o(1 + at + bt^2).$$

If α be the absolute coefficient of linear expansion, then the constant increment per degree is $\Delta\alpha/\Delta t$, and their relations to the constants a and b of the above formula can be ascertained at once by successive differentiation with respect to the temperature. Thus

$$\alpha = a + 2bt, \text{ and } \Delta\alpha/\Delta t = 2b.$$

The mean coefficient of linear expansion between 0° and $t°$ is, therefore, $a+bt$; but the true coefficient at any particular temperature t, and also the mean coefficient between any two temperatures whose mean is t, is $a+2bt$.

Hence, in order to be able to determine the true and mean coefficients, and the increment per degree, which together afford full information as to the nature of the expansion, it is only necessary to ascertain the constants a and b in the general expression above given for L_t. How this is achieved, by making observations for two intervals of temperature, will be explained in the next chapter, and particularly, as regards the necessary calculations, on page 1321.

As regards the cubical expansion, if the length L_t of an edge of the cube of the solid at $t°$, compared with its length L_o at 0°, be taken, as above, as

$$1 + at + bt^2,$$

then the volume of the cube at $t°$ (assuming homogeneity of the material of the substance, and equality of expansion throughout) will be $(1 + at + bt^2)^3$. On working this out, it is found that only the three first terms of the result, namely, $1 + 3at + 3bt^2$ or $1 + 3(at + bt^2)$, are of significant value, the rest involving the square or higher powers of a or b (a and b being to begin with only decimal fractions having several ciphers after the point), which do not influence the result. The cubical expansion coefficient is thus simply three times the linear coefficient.

The case may, indeed, be put more simply thus. If the coefficient of linear expansion be α, and the edge-length at 0° be 1, then at 1° it

becomes $1+\alpha$. The cube of this, $(1+\alpha)^3$, is $1+3\alpha+3\alpha^2+\alpha^3$, and only the first two terms, $1+3\alpha$, are of significance. That is, the coefficient of cubical expansion is 3α, or in other words three times the coefficient of linear expansion.

Variation of Linear Expansion with the Symmetry.—A crystal belonging to the cubic system expands equally in all directions, like non-crystalline substances such as glass, or heterogeneously crystallised substances such as metals. Hence a cubic, promiscuously finely crystallised, or non-crystalline substance has only one expression for its linear expansion. A sphere cut out of such an isotropic crystal remains a sphere on being heated or cooled, its radius as a rule increasing with rise of temperature. The interfacial angles of cubic crystals remain unaltered by variation of temperature.

The cubical expansion of such a cubic crystal or other isotropic substance is 3α, as already shown. For when the expression for the linear expansion is cubed, all other terms are found to be too small to affect the significant figures of the coefficient.

A crystal belonging to one of the optically uniaxial systems of symmetry, the tetragonal, hexagonal, and trigonal, expands in general differently in different directions, but there is this regularity in the differences, that the maxima and minima of expansion occur along the respective directions (or *vice versâ*) of the optic axis and any direction perpendicular thereto, along which latter infinity of directions lying in the equatorial plane the expansion is equal. Thus two expressions for the linear expansion, one for the direction of the axis and another for directions perpendicular thereto, are required in the case of a uniaxial crystal. Hence, a sphere cut out of a uniaxial crystal becomes an ellipsoid of revolution on heating or cooling, the axis of which is coincident in direction with the optic axis. All the faces of the crystal which are parallel (together with their edges of intersection) to the optic and thermal axis, or perpendicular thereto (the basal planes), remain unaffected in their angles of mutual intersection ; but the inclinations of faces oblique to the axis are altered. When the axis is the direction of maximum expansion these pyramidal or domal faces become steeper with rise of temperature, but when the axis is the direction of minimum thermal dilatation the form becomes a flatter one. The mode of measuring such angles at temperatures up to 120° was dealt with fully in Chapter XXVI. It was the study of such changes for the first time by Mitscherlich, in the case of calcite, that brought to light both the fact that such interfacial angles of crystals are dependent on the temperature, and indirectly the laws of the thermal dilatation of crystals. Mitscherlich caused the first really delicate goniometer, reading to ten seconds of arc, to be constructed by the then celebrated mechanician Pistor, for this very purpose, and with its aid showed that the rhombohedral angle of each of several fine rhombs of calc-spar from Eskifjördhr in Iceland was 105° 4′ at 10°, but became reduced to 104° 56′ at 110° C.

The cubical expansion of a uniaxial crystal is obtained by adding to the constants a and $2b$ for the axial direction twice the values of those constants for the equatorial direction. That is, if α represent the

coefficient for the former direction and a' that for the latter, then the cubical expansion is $a + 2a'$.

A crystal belonging to the optically biaxial systems, the rhombic, monoclinic, or triclinic, expands unequally in different directions, and there are two directions perpendicular to each other along which the dilatation is respectively a maximum and a minimum, while the direction at right angles to both, the normal to their plane, exhibits an intermediate amount of expansion. These three rectangular directions form the axes of a thermal ellipsoid of general triaxial character, analogous to the optical ellipsoid. A sphere cut from such a crystal becomes converted by change of temperature into an ellipsoid of this form. In the case of a biaxial crystal, therefore, three expressions for the linear expansion are required, one for each of these three axial directions. The three axes are only coincident with the crystallographic ones and those of the optical ellipsoid in the case of crystals belonging to the rhombic system, although even here the lengths in general have no relations. In the monoclinic system only one thermal axis is identical in direction with a crystallographic axis, the symmetry axis b, which is likewise an axis of the optical ellipsoid. The other two thermal axes lie in the symmetry plane, and although similarly rectangularly inclined have no necessary (although often a fortuitous) connection with the directions in that plane occupied by the optical axes. In the triclinic system the three rectangular thermal axes may have any orientation, consistent with the retention of their mutual perpendicularity. Consequently, only in the rhombic system do the pinakoidal forms all remain angularly unaltered at 90°. In the monoclinic system the clinopinakoid b {010}, the plane of symmetry, remains always at 90° to the orthopinakoidal forms, the mutual angles of which, however, change with the temperature.

The cubical expansion of a crystal, the thermal expansion of which is thus represented by a triaxial ellipsoid, is the sum of the three linear coefficients of expansion along the three axes. For when the expression for the expansion of the solid, the product of the three linear expansions along the three rectangular axes of the thermal ellipsoid, is examined, it is found (just as in the case of a homogeneous non-crystalline or isotropic substance already dealt with in detail) that only two terms in it affect the fourth significant figure in the coefficient of expansion, namely, the sums of the 3 values of a and of b respectively.

The practical determination of the thermal dilatation of crystals will be dealt with in the next chapter, as a new, highly important and useful experimental principle, that of measurement in wave-lengths of light, is involved, the method of the interferometer.

CHAPTER LVII

THE INTERFEROMETRIC DETERMINATION OF THE THERMAL EXPANSION OF CRYSTALS — GENERAL USE OF THE INTERFEROMETER IN FINE MEASUREMENT

The determination of the coefficient of expansion of so small a body as a crystal usually is obviously demands a very much more sensitive experimental method than is suitable for substances obtainable in greater mass. Such a delicate and refined method is that devised by Fizeau in the year 1864,[1] which utilises the production of interference fringes and employs them as a natural scale of half wave-lengths of light. This innovation has during the last few years been developed to a very important extent, the method or process being of wide application and generally known as "Interferometry," and the instrument employed as the "Interferometer."

The original process employed by Fizeau, for the determination of the thermal dilatation of crystals, depends essentially on the measurement of the difference of expansion of the crystal and of a small platinum tripod, composed of three screws of fine pitch, screwing through a little table on which the crystal is supported. This measurement is effected by observing the alteration of the thickness of the film of air between the upper plane surface of the crystal and the lower plane surface of a plano-convex lens supported over it by the three screw-legs of the tripod, on the tops of which the lens rests. Interference fringes are generated between the light reflected from the two surfaces, and when the thickness of the air-film separating the two alters, owing to the difference of expansion of the two substances forming the crystal and the tripod, the fringes also move, and for every fringe that passes a reference spot an alteration of thickness of the air-film at the spot has occurred equal to half the wave-length of the light employed. For the light derived from the second reflecting surface has to traverse the air-film twice, on its incidence and after its reflection, so that each alteration of thickness of the film equal to half a wave-length is equivalent to a whole wave-length of retardation or difference of path of this light behind the light derived from the first reflecting surface, thus corresponding to repetition of the same phenomenon

[1] H. Fizeau, *Compt. rend.*, 1864, *58*, 923, and 1866, *62*, 1133; *Ann. Chim. Phys.*, 1864, [4], *2*, 143, and 1866, *8*, 335; see also J. R. Benôit, "Études sur l'appareil de M. Fizeau pour la mesure des dilatations," *Trav. et Mém. du Bur. internat. des poids et mesures*, 1881, *1*, 1, and 1888, *6*, 1.

of light or darkness, the phases being similar. Hence, if an interference dark fringe were over the reference spot before the alteration of thickness, the next fringe would have replaced it over the spot at the completion of the alteration equal to a half wave-length. Whether a fringe (total extinction of light) or a bright interval (of no interference) is over the spot depends on the total retardation (difference of path), that is, that due to traversing the film plus the constant half-wave-length change of phase due to one reflection from a denser medium (the crystal) into a lighter (the air-film) medium, as explained in Chapter XLII. (p. 892) in connection with Newton's rings. Hence whole wave-lengths (even numbers of half wave-lengths) of retardation of one of the two beams of light behind the other, due to the extra double passage of film alone, correspond to the dark fringes and odd numbers of half wave-lengths to bright intervals. Fizeau employed sodium light, as the fringes are only produced in monochromatic light, and they are the sharper, and visible for greater thicknesses of the air-film, the more perfect the monochromatism.

Now, as is well known, sodium light corresponds to two lines of the spectrum, D_1 of wave-length 0·0005896 mm. and D_2 of wave-length 0·0005890 mm. The light waves from these two sources consequently periodically interfere, such so-called "secondary interference" causing intermittent disappearance of the interference bands as the thickness of the air-film regularly increases. Hence, although sodium light served Fizeau's purpose, care being taken to avoid the positions for maximum secondary interference, it is not an ideal light to use for interference work. Moreover, the original Fizeau apparatus does not lend itself to micrometric measurement, nor does it fulfil one of the conditions for complete interference of the rays of light, namely, normal incidence of the rays on the reflecting surfaces. Both these defects are corrected in an improved form of apparatus devised by Abbe and employed by Pulfrich,[1] but even this new form suffered from the fact that the telescope was arranged over the hot air-bath. This, and a few other inconveniences, have been corrected and eliminated in a later form of apparatus of more general application constructed for the author,[2] and employed in the determination of the thermal expansion of the crystals of the alkali sulphates, of the metals nickel, cobalt, and aluminium, and of the alloy of platinum with 10 per cent of iridium, of which alloy the interference tripod is constructed in the author's apparatus. Fizeau used platinum and Benoit (the apparatus otherwise being that of Fizeau) the same Pt-Ir alloy as the author, while Abbe and Pulfrich used steel or quartz. The apparatus has also been employed for the important determination of the thermal expansion of the fine porcelain of which air or other gas thermometers are constructed, and also of that of a variety of glasses. The experience gained with these determinations has enabled the dilatometer to be brought to such a state of perfection as to render its interferometer portion not only of particular value for the determination of the thermal expansion of crystals, but of

[1] *Zeitschr. für Instrumentenkunde*, 1893, 365.

[2] *Phil. Trans.*, A, 1898, *191*, 313; 1899, *192*, 455; *Proc. Phys. Soc.*, A, 1899, *65*, 161 and 306; 1902, *18*, 631.

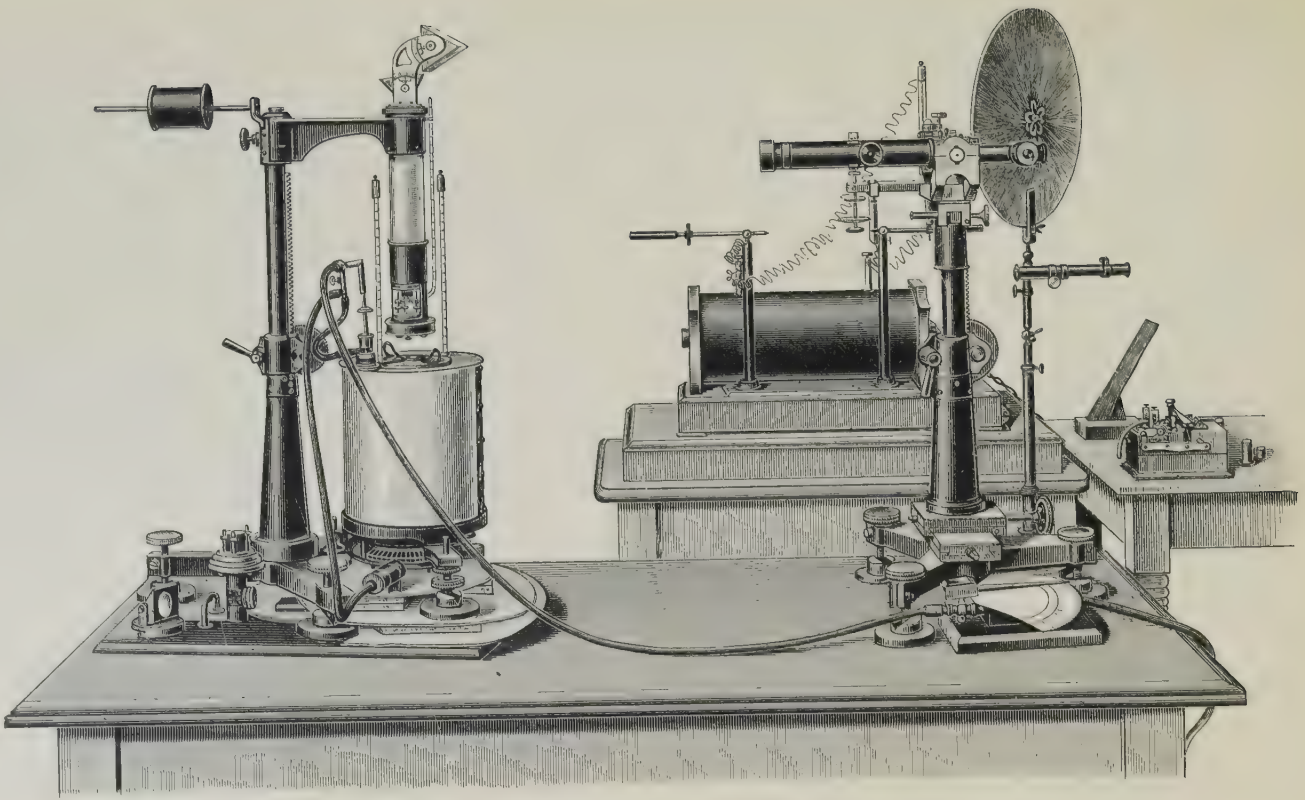


Fig. 887.—The Interference Dilatometer.

general convenience and application to the measurement of minute amounts of motion or short distances in general. It is constructed by Messrs. Troughton & Simms.

The Interference Dilatometer.—The dilatometer is shown in Fig. 887. It consists of two separate parts, mounted on a rigid slate table 5 feet 6 inches long to the right and to the left on independent pedestals, the left one carrying the interference apparatus in a suspended manner, so that it can be immersed in a cylindrical double air-bath of copper, lined outside with asbestos. Sections of the optical trains of the two parts are given in Figs. 888 and 889, and the lettering in the following description refers to these sectional drawings :

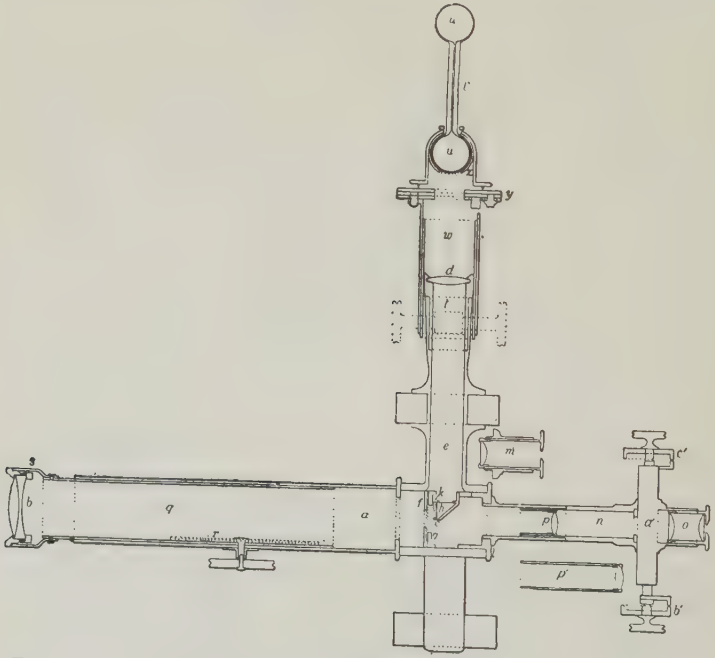


FIG. 888.—Section of Auto-collimating Telescope and Geissler Tube Attachment.

The right pedestal carries the observing telescope, *a* in Fig. 888, which is of auto collimating character, in order to ensure the normal incidence already referred to. It is shown in Fig. 890 in the manner in which the observer regards it from the end of the slate observing table. At the common focus of the objective *b* and eyepiece *m* or *n* the optical tube *a* is constricted by a diaphragm *g* with a fixed maximum aperture, which can be lessened to any extent by an iris diaphragm *f*; the right half of this circular aperture, as the observer stands at the right end of the long slate table looking through the telescope, is closed by a small totally reflecting prism *h*, which receives the rays from the source of light, which is an ordinary goniometer lamp when white light is used in preliminary adjustments, and a hydrogen, neon, mercury, or cadmium Geissler tube *uv* when observing in monochromatic light. The rays are concentrated on the little prism by a suitable lens *d* carried in an inner draw-tube *t* at the end of a short elbow tube *e* attached perpendicularly to the telescope

opposite the reflecting prism *h*, and the rays are reflected by the latter towards the objective *b*, the focus of which is adjustable by rack-and-pinion movement of the draw tube *q*. The side tube *e* carries the Geissler tube fitting as a readily detachable accessory, a tube *w* carrying it slipping over the collimator *e* and being adjustable by rack and pinion, which move an outer tube actually supporting the fitting *z*, in order to attain the right focus of the capillary *v*, the brilliantly illuminated section of which is the source of light; vertical and sideways adjustment of the end-on capillary is secured by two centring movements *y* for the tubular holder *z* of the supported wide limb of the H-shaped Geissler tube.

The telescope is adjustable for height by the stout rack and pinion of the pedestal, and for azimuth and altitude by fine motions; it is also adjustable in two rectangular directions by a pair of movements at the base of the pedestal. The aperture of the prism face looking towards the objective is restricted by the insertion of any one of a series of rectangular "stops," an oblong aperture in a metallic strip *k* provided with handle, which latter enables the strip to be pushed down into a slot cut for it in the optical tube, the strip nearly touching the prism face. The aperture of the stop usually employed is 3 by 2 millimeters, and it is cut out of the strip very close to one of the long edges of the latter, that one which when in position occupies the vertical diametral line of the whole iris aperture of the optical tube. This brings the little rectangular aperture, which may be regarded as the direct source of monochromatic light for the production of the interference bands, quite close to the axis of the telescope, thus practically securing normal incidence; for after returning from the interference apparatus the rays are arranged to arrive at the iris aperture just in the open half, so as to be visible to the observer looking through the eyepiece, and within a couple of millimetres of the origin-stop itself. The stop-aperture and its image are thus symmetrically arranged on each side of the optical axis of the telescope, very nearly touching each other and the optical axis bisecting the narrow strip between

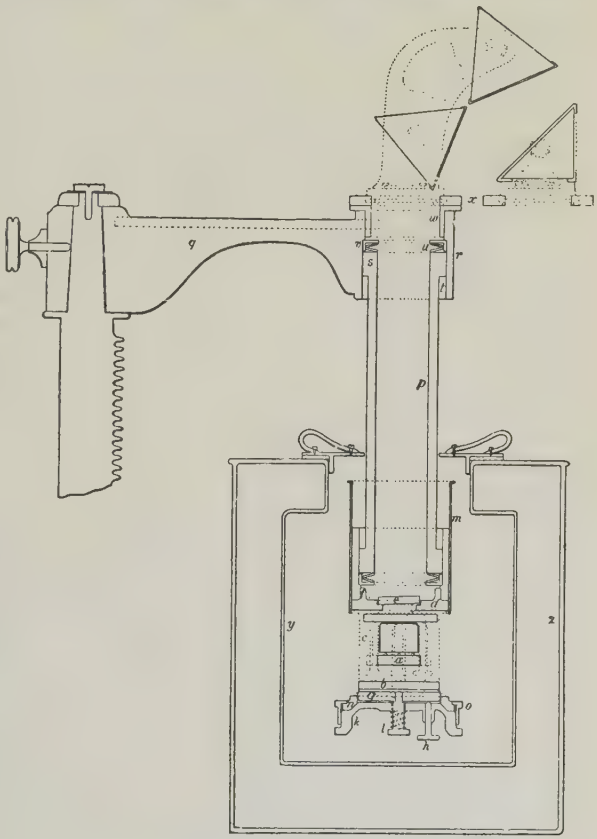


FIG. 889.—Section of Suspended Tube, Interference Apparatus, and Air-bath.

them. The stop-aperture is of course hidden from the observer by the prism case, which cuts off the right half of the circular field, and only the light forming the image of the rectangular stop is visible and passes to the eye, except for a trace of scattered light just adequate to render the open half of the field visible (see Fig. 904, image AB).

Two eyepieces are provided, one being a single-lens plano-convex eyepiece *m* magnifying four diameters. When this eyepiece is used and adjusted to its proper position the semicircular field (half of the iris aperture) just referred to is clearly focussed, being at the common focus of the objective *b* and eyepiece *m*, when the whole telescope is adjusted for parallel rays ; when the interference apparatus is in position the images of the rectangular stop are clearly focussed also, the image corresponding to the light reflected from the glass surface lying on the tripod screws being situated, as just indicated, quite close to the vertical diameter which sharply divides the dark almost invisible half from the more or less illuminated half of the circular field. The other eyepiece *n* is a positive two-lens (*o*) micrometer eyepiece carrying two vertical spider-lines, one moved horizontally parallel to itself by the milled-headed drum *b′* on one side of the micrometer box, while the drum *c′* on the other side moves both simultaneously. Each drum is divided into a hundred parts, and the function of this micrometer is to enable any interference band to be brought parallel to and to lie totally between the pair of vertical spider-lines, and so that both the position of this band and its distance from its adjacent fellows on either side may be accurately determined, as well as the width of a band, that is, the interval between two bands, in drum divisions ; the fraction of any band which may have partially passed the reference centre is at once afforded by these data. The central line between the two spider-lines is not the direct, but only the secondary reference position, the primary one being the centre of a minute silvered ring carried at the centre of the upper of the two interference surfaces (the lower surface of the glass plate laid on the tripod screws), in order that no error due to movement of the telescope may influence the results, the reference centre and the bands having the ideal common focus. The pair of spider-lines are set symmetrically, one on each side of the reference centre of the ring, so as to cut off minute equal chords on each side from the inner circular boundary of the ring, in order to determine the position of the centre of the latter, in a manner which will be clear from Fig. 891, which shows

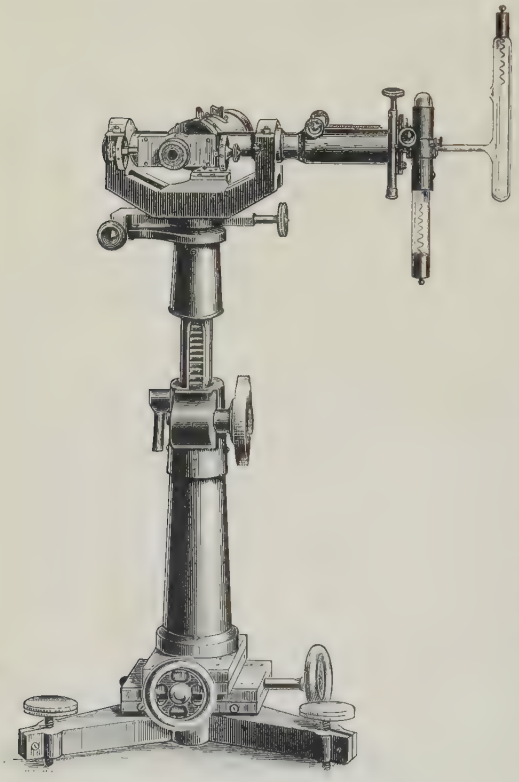


FIG. 890.—The Auto-collimating Telescope.

a typical field of interference bands as seen in the micrometer eyepiece of the telescope. For when this second eyepiece *no*, with an additional lens *p*, is used the field observed through it is no longer semicircular but circular, the reference silver ring being focussed (that is, the surface of the glass plate in contact with the tripod screws is in focus) instead of the iris diaphragm aperture, and when the interference apparatus is adjusted the bands are also visible and in focus. The combination of *o* and *p* with the objective *b* in fact converts the optical train into a telescope or a very low-power microscope focussing the interference surfaces between which the air-film is enclosed.

The attachment tube *n* of the micrometer eyepiece is somewhat long, in order that the additional lens *p*, converting the telescope into a very low-power microscope, may be accommodated in the elongation; its position is adjustable in the tube, several short inner tubes of different lengths being supplied, into the end of any one of which it screws, to enable the interference bands and the silver reference ring to be focussed clearly for different distances of the interference apparatus on its separate pedestal. One of these additional inner tubes is shown at *p'*. Usually only two are needed, one for close approximation of the two pedestals during adjusting operations, and another for the maximum separation during actual observations.

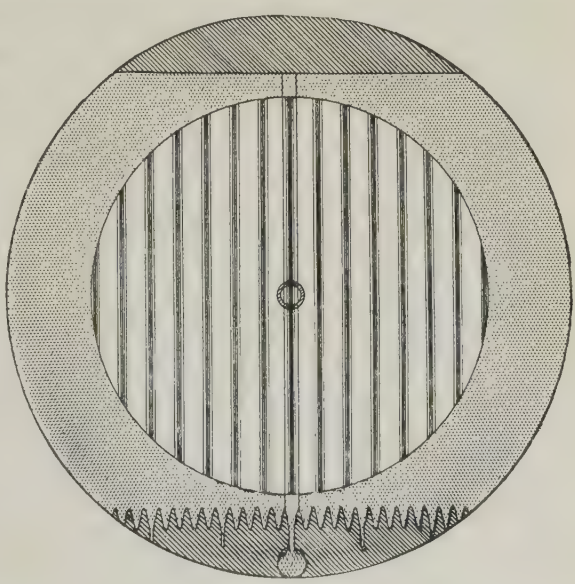
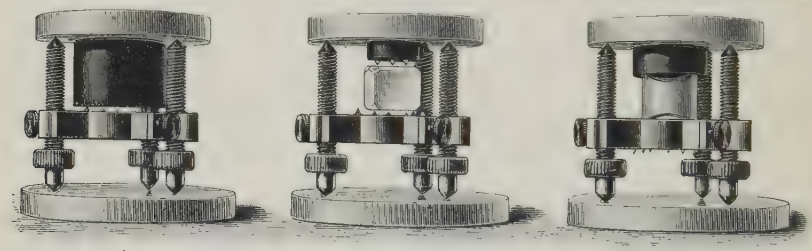


FIG. 891.—The Field of Interference Bands.

This second pedestal to the left is similar to the one on the right, being capable of considerable vertical elongation by the strong rack and pinion. It bears at its upper extremity a counterpoised arm, *q* in Fig. 889, from which the interference tube *p* is suspended. This is constructed in part of Berlin porcelain, in order to minimise conduction of heat from the interference chamber *c* which it carries at its lower extremity; the attachment between porcelain and metal is made by means of flanges *s* on the porcelain and annular springs *u* and securing-rings *v* and *t*, in such a manner that the difference of expansion is afforded free play. At the upper extremity a pair of refracting prisms are carried, adjustable for azimuth by the mode of attachment of their metal carrier-slide to an inner tube *w*, provided with a flange above, bearing the rabbeted guides for the carrier-slide of the prisms, this tube *w* rotating within the fixed tube *r* without vertical movement. The prisms are also each independently adjustable to minimum deviation, a pair of silver divided arcs, and indicators on the axes of the prism frames, being provided, best seen in Fig. 887, to enable this setting to be immediately recovered if ever it be disturbed for any other purpose. The refracting prisms are replaceable for adjustment purposes by a single large totally reflecting prism, shown separately to the right, and carried on a similar slider in a detachable upper part *x* of the flange of the inner tube *w*.

The angle of the two refracting prisms is such that the total deviation produced is exactly 90° for sodium light. They may be replaced if desired (although with less dispersion) by a single Hilger constant-deviation prism, affording a regular deviation of 90°. This alternative dispersing apparatus has proved very satisfactory in the interferometer devised by the author in connection with the Wave-Length Standard Comparator constructed under the author's supervision for the Standards Department of the Board of Trade, and described in the next chapter. Hence, its use can confidently be recommended in this or any other adaptation of the author's "interferometer." For the optical part of the dilatometer constitutes an interferometer of general applicability to the measurement of minute distances or quantities of motion.

The parallel beam of monochromatic light received by the dispersing prisms (or prism) from the telescope—the objective of which is filled with light from the little rectangular stop at its focus, in front of the small reflection prism—is thus deflected downwards at right angles along the axis of the interference tube p to the interference tripod a. The latter is supported in a detachable chamber c, which is attached by a screw-thread f carried by its perforated roof-plate d to the bottom of the interference tube. The greater part of the walls of this little chamber are cut away so as to leave three wide windows, through any one of which the interference tripod can be introduced. The roof d of the chamber is pierced by a central aperture an



(a) (b) (c)

FIG. 892.—The Interference Tripod of Platinum-iridium and three Modes of its Use.

inch in diameter, closed by a glass plate e to be referred to directly, as it forms part of the interference apparatus; it is held in a rabbet, through which a pair of small tilting screws are driven, in two positions 120° apart, in order to give the plate a slight inclination from normality to the vertical axis of the whole tube. The chamber terminates below in an adjustable floor g, the level of which can be adjusted by three screws h, which push it away from a base k rigidly attached to the bottom of the chamber n by a screw annulus o, a strong spring l holding the floor tightly down on the screws. The interference tripod a does not rest directly on the gun-metal floor g, but on a glass plate b, which is separated from g by a thick disc of asbestos. Conduction away of heat from the tripod is thus reduced to a minimum.

The interference apparatus, the essential part of the whole instrument, is shown two-thirds its real size at (a), (b), and (c) in Fig. 892, which represents three methods of its use. It consists of a tripod of platinum-iridium, the three legs of which are stout screws of fine pitch, with roundly pointed ends, and each furnished near the bottom with a milled head for rotating purposes, the fine adjustment of these screws being the means of adjusting the interference bands. The screws pass through three arms radiating from a thick table, also of solid platinum-iridium (10 per cent. of the latter metal being present in the alloy), and three small tightening screws of the same alloy secure the large screws in the adjusted positions at the right height above the table, the arms having each a saw-cut to facilitate the tightening. One surface of the table, the upper one at (c) in Fig. 892, is polished a true optical plane. The other

surface of the table, the upper one at (*a*) and (*b*) in Fig. 892, bears three concentric sets of raised points, each set consisting of three points of equal height, but the sets increasing in height as the centre of the table is receded from. These points are intended for the support of the crystal or other object the thermal expansion of which is to be determined, which requires to be furnished with two parallel surfaces, as shown at (*a*) in Fig. 892, one of the sets of points being found suitable to the dimensions of the lower of these two surfaces. The upper surface of the crystal or other object must be ground and polished a true plane. The largest size of object which it is convenient to employ is 25 millimetres (one inch) in diameter, and 12 millimetres in height (thickness). A cylinder of black glass of these dimensions is the object shown as under investigation at (*a*) in Fig. 892.

The height of the screws projecting above the table top is regulated so that the upper terminations of the screws are just higher than the upper surface of the object when the latter is resting on the table points. A thick circular glass plate is then laid over the screws, a film of air being thus left between the under surface of the plate and the upper surface of the object. These are the two surfaces which are caused to reflect the light waves which interfere. The lower surface of the object, when the latter is transparent, is ground just sufficiently to prevent any reflection, while both surfaces of the glass plate are polished truly plane, for the light has to traverse the glass plate twice in going to and returning from the object surface. Hence, there is a disturbing reflection from the upper surface of the glass plate, not required for interference purposes, and this is eliminated by making the two surfaces inclined at a minute angle, 35 minutes being the most convenient amount, instead of employing a parallel-surfaced plate. This small amount of inclination is just adequate to deflect the undesirable upper reflection to one side of the semicircular aperture *c* in Fig. 888, and behind the iris diaphragm *f*. The device introduces, however, a little dispersion, such a plate being really a prism of small angle, and this in turn is corrected by means of a duplicate wedge-plate oppositely arranged, the two being cut from the same carefully prepared plate having truly plane surfaces inclined at 35′. This countervailing wedge-disc is the smaller one, *e* in Fig. 889, of 27 mm. diameter already referred to as closing the aperture in the roof *d* of the interference chamber; the two little tilting screws in the rabbet supporting the disc serve to give it a slight inclination at right angles to the direction of the wedge and in a plane parallel to its edge. This direction is clearly marked on both plates by two engraved dots at that end of the diameter perpendicular to the edge of the wedge where the latter is thickest, and a single dot at the narrower end. Both the reflections from the countervailing wedge-disc are thus deflected out of the field, behind the iris diaphragm. Hence, the only light passing to the eyepiece through that diaphragm is that reflected from the upper surface of the crystal or other object under investigation, and from the lower surface of the large glass wedge-disc resting on the screws of the platinum-iridium tripod. This lower glass surface is the one which bears at its centre a miniature silvered ring, which serves as an excellent reference spot, the movement or position of the interference bands being measured with reference to the centre of the ring, as will be clear from Fig. 891.

In the not uncommon event, especially in the case of artificial crystals, of the surface of the crystal or other object not taking a good polish, the author places over it a disc of aluminium, the expansion of which is accurately known, an exhaustive series of determinations of the expansion of aluminium having been carried out by the author in the year 1898,[1] by using a block of the metal slightly over 12 mm. thick, similar to the black glass block shown at (*a*) in Fig. 892. Aluminium has three advantages, the first being that its expansion is 2·6 times as great as that of platinum-iridium. Hence, it is easy to select a disc of such thickness as will approximately compensate for the expansion of the platinum-iridium screws, and thus an immediate indication of the real degree of expansion of the crystal or other object is afforded by the

[1] *Phil. Trans. Roy. Soc.*, A, 1898, *191*, 360.

alteration of the thickness of the air-film, instead of merely the differential expansion of object and screws being observed. No attempt is made at absolute compensation, the actual expansions of the aluminium and screws being of course taken into account in the calculations; but it is often a convenience to see at once the kind of expansion that is occurring, and in the occasional cases of contraction the unusual fact is at once indicated. In the second place, the surface of aluminium just takes that not too brilliant degree of polish as causes the reflection to be of about the same intensity as the partial reflection from the lower surface of the glass cover-wedge. Thirdly, aluminium is particularly light, and does not compress the crystal appreciably. Such a case is that shown at (*b*) in Fig. 892. A crystal is represented standing on the intermediate set of three points of the tripod table, and an aluminium disc, also furnished below with three points, is seen resting in turn by the latter on the crystal. Still another case of the use of the aluminium disc is shown at *c*, where a specimen of Bayeux porcelain, a piece of tube 12 millimetres high, very inconvenient in itself for the production of interference bands, is seen as arranged for a determination of its thermal expansion; the planely ground upper and lower parallel terminations of the piece of tube were cut away extensively at three places in each case, to enable the porcelain to rest by three-point contact on the platinum-iridium table (the other surface, not furnished with points, of the table being employed in this case), and to permit an aluminium disc to rest in a similar manner on the porcelain.

In making a determination of expansion the interference tube carried by the second pedestal is immersed in the inner chamber of the double air-bath of copper (the outside covering of asbestos of which retards loss of heat by radiation), until about one-third of the porcelain tube is below the level of the top of the bath, the interference chamber then occupying a position slightly below the centre of the bath. The inner bath *y* in Fig. 889 is closed by a lid, fitted together in two parts when the interference apparatus is in position. Two thermometers are inserted through tubulures into the inner bath *y*, and a Muencke thermostat into the outer bath *z*, which with the aid of a Stott governor and a tap with long lever arm moving over a divided quadrant-arc, seen in front of the right pedestal in Fig. 887, enable an excellent control to be obtained over the temperature, by affording delicate regulation of the gas supply to the Fletcher ring burner arranged beneath the air-bath. The actual temperature of the interference apparatus, however, is measured by a special thermometer suspended in the inner bath alongside the interference tripod, and bent at right angles just above the bulb, in order that the latter may actually lie on the platinum-iridium table quite close to the crystal or other object, where it is secured by tying it to the nearest leg of the tripod with a silk thread.

The Determination of Thermal Expansion.—The interference apparatus is first adjusted to afford a suitable field of bands, of the nature shown in Fig. 891. During this and all other preliminary adjustment the left pedestal is brought up towards the right one (which always remains near the right observing end of the slate table), so that the upper prism of the dispersing apparatus is about an inch removed from the objective end of the telescope. When the colourless glass 35′ wedge-disc is laid over the screws of the platinum-iridium tripod, the crystal or other object under investigation with or without the aluminium disc being already in position on the table of the tripod, the height of the screws projecting through the table is so regulated that an apparently parallel-surfaced film of air of half a millimetre or slightly more thickness is left between the crystal or aluminium surface and the lower glass surface. The large total reflection prism should then be placed in position at the top of the interference tube instead of the two refracting prisms, and the images of the little rectangular stop in

front of the small reflecting prism of the telescope are reviewed in white light, using the ordinary goniometer lamp and the common eyepiece *m*, as reflected from the two surfaces in question which afford the interference. Three other images are also seen, derived from the second surface of the glass wedge-disc and the two surfaces of the countervailing wedge-disc, and all four images derived from the two wedge-discs are adjusted *en échelon* to occupy the corners of a rhombus; for then the four vertically arranged spectra corresponding (produced when the two refracting prisms are reinstated in position) will not overlap and interfere, and will in fact be separated to an extent which will enable the iris diaphragm to shut off all but the one from the surface next to the crystal or aluminium surface, which alone is wanted. This right one may be readily identified, for it is one of the two which move when the glass disc lying on the screws is touched; when the disposition of the wedge is known, as it always will be, never altering, the correct one of the two is at once known. For it will always be either the right or left of these two, according as the thicker part of the wedge is known to be arranged.

The image from the surface of the crystal, black glass demonstration block, or other object, or the aluminium disc, may also be identified as a fifth independent image, some distance from the others unless the parallelism of the surfaces has been well attained, by touching the object for a moment, which causes the image to tremble; and this fifth image is then made by adjustment of one, or, if necessary, two of the platinum-iridium screws, to approach the one derived from the surface of the wedge-disc which has just been recognised, and eventually partially to overlap and almost cover the latter. Fig. 904, representing the similar five images afforded in the interferometer of the wave-length comparator, will render the arrangement clear, the only difference being that the spectra are horizontal in that apparatus and vertical in the dilatometer interferometer now under discussion, and that the pair of images from each disc are in the same vertical line with each other instead of being *en échelon*. Generally it will be found that these two images relevant to the interference (A and B in Fig. 904) should be at precisely the same vertical height in the field, and that they should overlap horizontally to about four-fifths of their extent, in order to secure the conditions for the production of vertical interference bands of a width equal at least to one hundred drum divisions of the micrometer eyepiece. If now (1) the large totally reflecting prism be replaced by the two refracting prisms, (2) the common eyepiece *m* be replaced by the special one *n* provided with micrometer, the lens *p* being in its shorter draw-tube, and (3) the goniometer white-light lamp be replaced by the hydrogen Geissler tube excited by the induction coil (or by a transformer giving a suitable high tension alternating current, with the aid of a converter if the supply current be continuous, with a carbon filament lamp resistance in series with the primary of the transformer), the interference bands will themselves be seen conveniently spaced and vertically arranged as expected (Fig. 891), as dark rectilinear bands on a brilliantly illuminated ground in the colour corresponding to the wave-length for

which the telescope had been adjusted for altitude, generally that corresponding to the red line of hydrogen. If the bands, however, do require some slight adjustment for width or parallelism to the spider-lines, it can be readily attained by slight further manipulation of the tripod screws. The altitude adjustment screw of the telescope carries a sharp edged disc indicating on a vertical scale suspended alongside; the scale readings for the adjustment of the spectrum lines most used, to the centre of the field, have once for all been determined, with the aid of a special slit-stop temporarily replacing the oblong stop *k*.

The bent thermometer is now attached in its place. The left pedestal, with the whole of the apparatus suspended therefrom, is then moved to a suitable marked position about four feet away (measuring from the central vertical axis of the one column to that of the other) from the right pedestal carrying the observing apparatus, in order that no heat may reach the latter, large mica screens being also erected between the two parts of the apparatus, and between the air-bath and the dispersing apparatus, when all is ready, to assist still further in preventing any heating of the optical parts. The left pedestal is mounted on a mahogany base-board, covered below with broadcloth to facilitate sliding, and supplied with two handles to enable it to be drawn gently and steadily into the desired marked position at the left end of the smooth slate table without any disturbance of the interference apparatus.

The interference bands should now be reviewed after the transference, with the movable lens *p* of the micrometer eyepiece readjusted in the proper (longer) draw-tube corresponding to the longer-focus position. The suspended tube is then gently raised by the pedestal rack and pinion, while the air-bath is placed in position on its annular support over the ring of gas burners; the tube is then as delicately lowered into its correct position in the bath, as indicated by a mark on the pedestal lengthening shaft; and the lid, thermometers and thermostat, together with asbestos and mica screens to ward off draughts and the convection currents, all fitted into their proper places. The bands are then finally reviewed, in order to be sure that no derangement has occurred, and their position for the ordinary temperature, read on the bent thermometer, is determined after a reasonable interval has elapsed for temperature equilibrium to have been established. That is, if a band does not happen to be placed exactly between the pair of vertical spider-lines, and over the reference centre of the silvered ring carried by the under surface of the glass cover-wedge, as shown in Fig. 891, which will only rarely occur, the fraction of a band, the interval between the reference spot and the centre of the nearest band, requires to be determined. To do this we measure the width of a band in drum divisions (the interval between the centres of the two bands nearest to the reference centre), and the distance of the next band (the distance of the reference centre from the centre of the nearest band) also in drum divisions, when the quotient of the latter over the former is either the fraction of a band required, or the complementary fraction, according to the direction in which the bands move when the heating commences. The object in producing rectilinear bands—

rather than circular interference rings or the curved fringes afforded by the lenticular cover-glass of Fizeau—is to render them suitable for such micrometric measurement, and to obtain a field containing several straight dark bands as narrow parallel lines separated by broad brilliantly illuminated interspaces, so that the distance between the blackest central part of two adjacent bands can be determined by measuring it between five or six successive pairs of bands, the average of which will give a very accurate quantity for the true " width " of a band. As the drum is divided into a hundred parts, and as matters are so arranged that a convenient width to which to adjust the bands, which still enables about a dozen of them to be visible in the field at once, corresponds to one drum revolution, the interval between two consecutive bands can thus be subdivided into a hundred parts.

Now each pair of consecutive black interference bands correspond to a difference of thickness of the air-film at the two positions where they are produced of half the wave-length of the light which is interfering. For the light has to traverse over the distance between the two surfaces reflecting the light; once in approaching the second surface, and again in returning therefrom after the reflection thereat. Hence, a half wave-length of change of thickness of the air-film corresponds to the whole wave-length of retardation, of the light reflected from the lower of the two surfaces (crystal) behind that reflected from the upper one (glass), necessary for identity of phase of the light, and therefore for the repetition of the light (a bright band) or darkness (a dark band) started with. If either of the reflecting surfaces be moved in the direction of its normal, keeping it parallel to itself, the bands also move parallel to themselves, and for every black band which has moved past the centre of the reference ring the moving surface has actually travelled through a distance (opposite this spot) equal to the half wave-length of the light employed to produce the bands. The diameter of the silver ring is arranged to be just a trace greater than the separation of the spider-lines, so that a little segment can be arranged to show outside each (see Fig. 891) when the spider-lines are " adjusted to the centre." The gross unit of the interferometer scale, formed by the black bands themselves, is thus the half wave-length of the monochromatic light employed to produce the bands, and this being divisible into 100 parts by the micrometer, the actual unit is the two-hundredth part of the wave-length. The observer can actually divide the distance between the two consecutive bands readily by the eye and judgment alone into ten parts, even without the micrometer.

The light employed for all ordinary purposes is that of the red hydrogen ray Hα, the C of the solar spectrum. The wave-length of this light is 0·0006562 millimetre or $\frac{1}{38,710}$ of an inch, and the half wave-length consequently 0·0003281 mm., or $\frac{1}{3048}$ of a millimetre, or $\frac{1}{77,419}$ of an inch. The one-hundredth part of this is the unit of measurement of the instrument, namely in round numbers, the three-hundred thousandth part of a millimetre or the eight-millionth part of an inch.

If the air-film between the closely adjacent reflecting surfaces were of equal thickness throughout—that is, if the truly plane surfaces were

strictly parallel—alternate fields of the brilliant monochromatic light and of jet-black darkness would be observed as the distance of separation of the surfaces was varied by moving one of the surfaces normally and parallel to itself. But when the air-film is made slightly wedge-shaped, by tilting one of the discs, then rectilinear interference bands (lines of extinction) are produced, parallel to the edge of the wedge, the width of which diminishes as the tilt increases and which rotate if the position of the edge of the air-wedge (that is, of the direction of tilting) be altered.

The thickness of the air-film should theoretically not matter if the light were absolutely monochromatic, that is, if the spectrum line corresponding to it were single and absolutely unresolvable into a double line or a triplet by extreme dispersion. But the only line that has yet absolutely resisted resolution is the red line of cadmium vapour, wave-length 0·0006438 mm., and with light corresponding to this wave-length the bands can still be seen when the surfaces are a decimetre apart. With light of the wave-length of the green mercury line, wave-length 0·0005461 mm., the interference bands are still visible for a separation of the surfaces of between one and two centimetres. With red C-hydrogen light, the surfaces must not be further apart than about three millimetres. Between half a millimetre and a millimetre is the best distance of separation for brilliant bands either in the red C-light, or in the greenish-blue F-hydrogen light of wave-length 0·0004861 mm. Both these lines are close doublets.

The author has also been experimenting lately with Geissler tubes of neon, the yellow-line radiation of which, of 0·0005852 mm. wave-length, is also homogeneous to a remarkable degree of perfection (although it is not yet quite certain that it is so unresolvable as the red line of cadmium), and the yellow light of which gives splendid illumination ; neon tubes are also convenient in working at the ordinary temperature, like hydrogen tubes, and thus requiring no extraneous heating, whereas cadmium tubes require to be heated to about 200-250° C.

The author has also used vacuum tubes of helium and argon, the light of the yellow helium line D_3 being particularly suitable for the production of brilliant bands. Its wave-length is 0·0005876 mm., and as regards resolution it is either a single line or a very close doublet, so close that secondary interference is not perceptible. It also goes without saying that instead of Geissler vacuum tubes containing cadmium or mercury, the enclosed cadmium-vapour arc lamp or mercury-vapour lamp of Dr. Sand (Fig. 722) constructed of quartz glass, or the special form of Cooper-Hewitt mercury lamp shown in Fig. 722*b*, may be used, and are very efficient and convenient sources of monochromatic light. They are described on pages 971 and 973.

The measurement of the position of the bands having been made, and the temperature of the inner bent thermometer read by a small telescope on a stand near the first pedestal, seen in Fig. 887, and which also carries a circular screen to shade off the glare from the Geissler tube, the double ring of Bunsen gas jets is ignited and turned very low, in order to raise the temperature of the bath very slowly. The bands are carefully observed, the Ruhmkorff coil being intermittently actuated

every few seconds as the bands begin to move. The passage of each band is noted as it passes between the vertical pair of spider-lines; indeed the author finds it the safest course to note every quarter of a band, being then sure that no band has escaped being counted. When the temperature approaches the neighbourhood of the first higher limit, usually about 60° C., it is carefully controlled by means of the graduated gas tap, and eventually brought to constancy, at which it is maintained for a full hour, the bands having almost simultaneously ceased to move. The temperature of the bent thermometer is then again read, and if the last band does not happen to have stopped in the central adjusted position, but has gone somewhat further, as usually occurs, its position with respect to the reference spot and the band width is determined, in order that the last fraction of a band may be calculated. The gas may then be turned higher and the temperature again slowly raised to the higher limit, about 120°, the bands which effect their traverse during the process being counted as before. Constancy is again brought about for an hour at this higher limiting temperature, and the last fraction of a band measured when the bands have settled into perfect repose.

The operations should take a minimum of five hours, but need never exceed seven hours altogether. By raising the temperature thus slowly the chance of cracking the crystal is minimised, and the temperature of the platinum-iridium tripod and its contents follows closely after that of the inner air-bath. It is much more satisfactory thus to watch the process throughout, than to make observations with several wave-lengths and obtain the number of bands by calculation, a method described by Pulfrich (*loc. cit.*). After the apparatus has cooled down again the lengths of the platinum-iridium screws above the table, the thickness of the crystal, and that of the aluminium disc when one is used, are to be measured by the thickness measurer *in situ*, under the reference spot.

Determination of Thickness.—A convenient and very accurate thickness measurer is shown in Fig. 893.

It consists of a vertical rod *a* with a silver millimetre scale *b*, suspended from gimbals *c* in a nearly counterpoised manner, with the aid of a cord passing over a pulley *d* and a weight *e*. The rod terminates below in a rounded agate point, which is lowered on to the upper surface *f* of the object *g*, the thickness (height) of which, above a thick glass plate *h* intended for its reception, is to be measured. The scale is read by a low-power microscope *k*, provided with a micrometer eyepiece *l*, the drum *m* of which is divided into 100 parts. The scale is divided directly into fifths of a millimetre, and two rotations of the micrometer drum correspond to a scale division, so that one rotation thus occurs for each tenth of a millimetre. Hence, each drum division indicates the thousandth of a millimetre. In the author's varied experience of all modes of fine measurement, the thousandth of a millimetre is the smallest unit attainable with accuracy by mechanical means. For any higher accuracy recourse must be had to a scale of interference bands. The thousandth of a millimetre is just adequate for the determination of thickness. For it is the ten- (or twelve-) thousandth part of the ten (or twelve) millimetres of thickness given to the object under determination for expansion, and this fraction of the total expansion, which an error of one drum unit would entail, is smaller than the experimental error of the whole process. It is not necessary that the initial thickness should be determined to the unit of the interference method, and it is mechanically impossible.

The whole thickness measurer is supported on a solid base *n*, in which a circular shallow recess is cut for the reception of the glass base-plate *h*, which rests on three points (the ends of three screws) carried in the recess ; a curved pillar *o* carries in front guides for the rod, and behind supports the winch for raising or lowering the scale by means of the cord, while a forward arm *p* bears the microscope. The instrument was made by Troughton & Simms, and a similar instrument, but with a different gimbal arrangement and other details, is also constructed in an admirable manner by Zeiss.

On releasing the bent thermometer, and removal of the interference tripod and its contents, except the large glass cover-wedge (which is lifted up while the tripod is removed, and then left behind in the chamber, inverted so as not to injure the little silvered reference ring), the tripod is carried without disturbance straight to the thickness measurer, on the glass-plate base *h* of which it is placed, with the centre of the aluminium disc (if used, or crystal or other object if not) under the agate point of the suspended rod *a*.

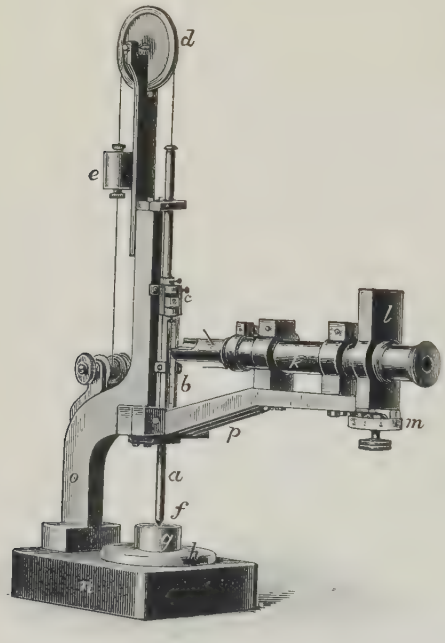


FIG. 893.—The Thickness Measurer.

When the height of the centre of the top surface of the aluminium disc, over which the reference ring of the wedge-disc had been situated, and of that of the crystal has been taken the disc or crystal (or both, one after the other) is removed, and finally the height of the upper platinum-iridium surface is taken. If the three points of any of the three sets are used, their mean difference from (height above) the surface is known by having determined it for each set once for all. The difference of the first two heights gives the thickness l_a of the aluminium (if used), and that between the second and third heights gives the thickness L_{t_1} of the crystal. The height of the plane of the tops of the platinum-iridium screws is already known from previous measurements ; but it may be freshly determined also at the centre with the aid of a glass disc with truly parallel surfaces and of known thickness laid over them. The difference between this and the height of the table top or the mean height of the set of points used is the length *l* of the screws, while the difference from the height of the aluminium (or crystal) top surface is the thickness *d* of the air-film. These thicknesses, thus determined all through under the very spot where the reference ring had

been, are the original lengths actually expanded, according to the indications of the movement of the interference bands at the reference spot, and are those used in the calculations.

An example taken at random from actual measurements with the alkali sulphates will render the process quite clear. It refers to a crystal of cæsium sulphate along the direction of the morphological axis *b*, the crystal having had two truly plane broad surfaces ground on it perpendicular to this direction, by one of which it rested on the tripod table, and on the upper of which the aluminium disc rested.

MEASUREMENTS OF THICKNESS.

	Millimetres.	Millimetres.
Height of top of glass disc	40·857	..
Known thickness of glass disc	6·117	..
Height of screws	34·740	$d = 0·145$
,, ,, top of aluminium compensator	34·595	$l_a = 5·253$
,, ,, ,, crystal	29·342	$L_{t_1} = 8·379$
,, ,, ,, tripod table	20·963	$l = 13·777$

By making the determinations for two different intervals we are enabled to calculate not only the mean coefficient of expansion, but also the increment per degree of temperature, as the coefficient varies, usually increasing regularly, with rise of temperature.

The Calculations of Thermal Expansion.—The coefficient of thermal expansion is signified by a, and it has already been shown that the expression for the actual coefficient at any temperature t, as also for the mean coefficient between any two temperatures the mean of which is t, is

$$a = a + 2bt.$$

The mean coefficient of expansion between 0° and $t°$ is, however,

$$a + bt.$$

The data afforded by observations of the positions of the interference bands at three adequately separated temperatures, and of the number of bands passing the reference point during the intervals between these temperatures, together with a knowledge of the original thicknesses of the block of crystal and of the aluminium compensator, and the length of the platinum-iridium screws projecting above the tripod table or its raised points, are ample to enable the two constants a and b to be calculated. For it is only necessary to insert respectively in three equations of the form

$$L_t = L_0(1 + at + bt^2)$$

the known values of the three temperatures and the lengths (thicknesses) of the crystal block at those temperatures, and to solve the three equations thus provided, for the three unknown quantities L_0, a, and b.

The solution of these equations furnishes expressions for the three required quantities of the forms

$$a = \frac{\theta}{L_0},\ b = \frac{\phi}{L_0},\ \text{and}\ L_0 = L_{t_1} - \theta t_1 - \phi t_1^2,$$

in which θ and ϕ are terms involving the differences of the lengths, L_{t1}, L_{t2}, L_{t3}, at the three temperatures t_1, t_2, and t_3, and the sums and differences of these temperatures.

The actual expressions for θ and ϕ employed throughout the observations were :

$$\theta = \frac{(t_1+t_3)\,(L_{t2}-L_{t1})}{(t_2-t_1)\;\;(t_3-t_2)} - \frac{(t_1+t_2)\,(L_{t3}-L_{t1})}{(t_3-t_1)\;\;(t_3-t_2)},$$

$$\phi = \frac{L_{t3}-L_{t1}}{(t_3-t_1)\,(t_3-t_2)} - \frac{L_{t2}-L_{t1}}{(t_2-t_1)\,(t_3-t_2)}.$$

A correction is required for the alteration of the wave-length by the large change of temperature, and for any appreciable change of atmospheric pressure during the observations. The effect of the latter is almost negligibly minute, but the barometer should be read at the time of taking each of the three temperatures, in order to be able to use the correction if necessary ; and as the correction is included in the same formula as that for temperature it is best always to apply it. The effect of change of temperature on the wave-length is, however, such as to require a quite serious correction, amounting in some ordinary cases in the author's investigations to nearly half a band, and when the expansion of the platinum-iridium tripod screws was being determined—when the air-film was the thickness of the whole 12 millimetres of screw length employed (green mercury light having been used, hydrogen light not affording bands at such long intervals), the lower reflection being directly that of the polished platinum-iridium table top (the side without points) the correction amounted to as much as $3\frac{1}{2}$ bands. Hence, this is an important matter requiring careful attention. The most satisfactory formula is due to Pulfrich,[1] and is as follows :

$$f' = f + d(t_2-t_1)\cdot\frac{b_1}{760}\cdot\frac{1}{1+\alpha t_1}\cdot\frac{1}{1+\alpha t_2}\cdot 2^{\frac{(n-1)\alpha}{\lambda}} - d(b_2-b_1)\cdot\frac{1}{1+\alpha t_2}\cdot 2^{\frac{n-1}{760\lambda}},$$

where f' is the corrected number of bands, f the observed number, d the thickness of the air layer, t_1 and t_2 the limiting temperatures, and b_1 and b_2 the corresponding barometric pressures, α is the coefficient of expansion of air, 0·00367, and n the refractive index of air for the wave-length λ of the light employed. The logarithmic values of $2^{\frac{(n-1)\alpha}{\lambda}}$ and $2^{\frac{n-1}{760\lambda}}$ can be found once for all ; they are respectively 3·59901 and 3·15353. The logarithms of the factors $\frac{b_1}{760}$, $\frac{1}{1+\alpha t_1}$, and $\frac{1}{1+\alpha t_2}$ can be extracted directly from Landolt's tables. Hence, the expression, although apparently long and troublesome, lends itself to very easy computation.

With regard to the sign of the correction, the signs given in the above formula for the temperature and pressure portions are the correct ones for use in all cases where the result of the increase of temperature is to effect

[1] *Zeitschrift für Instrumentenkunde*, 1893, 456.

an increase in the separation of the two reflecting surfaces, as in the determination of the expansion of the tripod screws. For in such cases the effect of change of temperature is to cause the observed number of bands to be less than it would be if such a change did not occur. The contrary is the case when the thickness of the air layer diminishes, as in the determination of expansion of a crystal or other object supported on the tripod table and the expansion of which is greater than that of the screws; and in all cases involving the use of the aluminium disc, except in the few cases of contracting substances. In all these cases of a thinning air-film the signs of the temperature and pressure portions of the above formula should be respectively − and +.

The data and calculated results for the thermal dilatation of a crystal of potassium sulphate may be taken as a concrete example. The crystal employed had two truly plane parallel surfaces ground on it a little over a centimetre apart, and perpendicular to the rhombic crystallographic axis *a*, so that the dilatation was determined along this direction.

THERMAL DILATATION OF POTASSIUM SULPHATE ALONG AXIS *a*.
EXPERIMENTAL DATA.

Lt_1	Length (thickness) of crystal block	10·355 mm.
l_a	Thickness of aluminium disc	5·237 mm.
l	Length of platinum-iridium screws above table	15·786 mm.
d	Thickness of air-film	0·194 mm.
t_1	Initial temperature	17·2°
b_1	„ pressure	766·5 mm.
t_2	Intermediate temperature limit	56·4°
b_2	„ pressure	765·0 mm.
t_3	Final temperature limit	96·6°
b_3	„ pressure	763·5 mm.
$\lambda/2$	Half wave-length of C-hydrogen light used	0·0003281 mm.
$a = a + 2bt$	Mean coefficient of linear expansion of platinum-iridium between any two temperatures of which the mean is t	$10^{-9}(8600 + 4{\cdot}56t)$
	Similar mean coefficient for aluminium	$10^{-8}(2204 + 2{\cdot}12t)$
f_2	Number of interference bands between t_1 and t_2	43·90
f_3	„ „ „ t_1 and t_3	90·42
f'_2	Corrected number of int. bands between t_1 and t_2	43·88
f'_3	„ „ „ t_1 and t_3	90·38

The two last quantities f'_2 and f'_3 were obtained by applying the correction referred to on the previous page to the observed numbers of bands f_2 and f_3, which effected their transit during the two respective temperature intervals. The correction in the two cases amounted to −0·02 and −0·04 respectively.

CALCULATED ACTUAL AMOUNTS OF EXPANSION.

$$\text{Diminution of thickness of air-layer} = \begin{cases} f'_2\lambda/2 = 0{\cdot}0143970. \\ f'_3\lambda/2 = 0{\cdot}0296540. \end{cases}$$

$$\text{Expansion of tripod screws} \begin{cases} \text{For 1st interval} = l\left[10^{-9}\left(8600 + 4{\cdot}56\,\frac{t_1+t_2}{2}\right)\right](t_2 - t_1) = 0{\cdot}0054256, \\ \text{„ 2nd „} = l\left[10^{-9}\left(8600 + 4{\cdot}56\,\frac{t_1+t_3}{2}\right)\right](t_3 - t_1) = 0{\cdot}0110887. \end{cases}$$

$$\text{Expansion of aluminium disc} \begin{cases} \text{For 1st interval} = l_a \left[10^{-8} \left(2204 + 2{\cdot}12 \frac{t_1 + t_2}{2} \right) \right] (t_2 - t_1) = 0{\cdot}0046848, \\ \text{,, 2nd ,,} = l_a \left[10^{-8} \left(2204 + 2{\cdot}12 \frac{t_1 + t_3}{2} \right) \right] (t_3 - t_1) = 0{\cdot}0096523. \end{cases}$$

$$\text{Preponderance of expansion of screws over disc} = \begin{cases} 0{\cdot}0007408 \text{ for 1st interval.} \\ 0{\cdot}0014364 \text{ for 2nd interval.} \end{cases}$$

As the effect of the expansion of the screws is to increase the thickness of the air-film, while that of the dilatation of the crystal is to thin the film, the full effect due to the crystal is not apparent, so the above two quantities are to be added to $f'_2\lambda/2$ and $f'_3\lambda/2$ respectively, in order to arrive at the expansion of the crystal.

$$\text{Expansion of crystal} = \begin{cases} L_{t_2} - L_{t_1} = 0{\cdot}0151378. \\ L_{t_3} - L_{t_1} = 0{\cdot}0310904. \end{cases}$$

Calculated Coefficient of Linear Expansion.

$$\theta = 0{\cdot}000\ 375\ 23.$$
$$\phi = 0{\cdot}000\ 000\ 148\ 5.$$
$$L_0 = 10{\cdot}3485.$$
$$a = 0{\cdot}000\ 036\ 26.$$
$$b = 0{\cdot}000\ 000\ 014\ 4.$$

That is, the mean coefficient of expansion of potassium sulphate along the direction of the axis a, between 0° and t°, is

$$a + bt = 0{\cdot}000\ 036\ 26 + 0{\cdot}000\ 000\ 014\ 4t;$$

and the true coefficient α of linear expansion at t°, or the mean coefficient between any two temperatures the mean of which is t, is

$$\alpha = a + 2bt = 10^{-8}(3626 + 2{\cdot}88t).$$

The result of this particular determination which has formed our example was confirmed by seven others, four different crystals being employed, all perpendicular to the axis a, and two determinations on different days were carried out with each. The final result was almost identical with that of our example, illustrating the extreme accuracy of the method, namely,

$$\alpha_{K_2SO_4,a} = 10^{-8}(3616 + 2{\cdot}88t) = 0{\cdot}000\ 036\ 16 + 0{\cdot}000\ 000\ 028\ 8t.$$

The expansion of the aluminium disc was determined by the ordinary Fizeau method shown at (*a*) in Fig. 892, a cylindrical block, with two parallel truly plane-polished normal end-surfaces 12 millimetres apart and 25 mm. in diameter, being prepared from the same casting from which all the aluminium discs were cut. It rested on the outer set of three points of the platinum-iridium table during the determination. The following data concerning the calculation will serve as an example of an ordinary Fizeau determination with the author's dilatometer :

Dilatation of Aluminium Data.

Thickness of aluminium block, $Lt_1 = 12{\cdot}188$ mm.
Length of platinum-iridium screws above table points, $l = 12{\cdot}400$ mm.
Thickness of air layer, $d = 0{\cdot}212$ mm.
Temperatures, $t_1 = 10{\cdot}1°$, $t_2 = 68{\cdot}9°$, $t_3 = 123{\cdot}4°$.
$t_2 - t_1 = 58{\cdot}8$, $t_3 - t_1 = 113{\cdot}3$.
Pressures, $b_1 = 754$, $b_2 = 754{\cdot}8$, $b_3 = 756$ mm.
Number of transited bands, $f_2 = 30{\cdot}35$, $f_3 = 60{\cdot}32$.

Corrections for air refraction, $-0{\cdot}04$, $-0{\cdot}06$.

Corrected number of bands, $f'_2 = 30{\cdot}31$, $f'_3 = 60{\cdot}26$.

Half wave-length of C-hydrogen light employed, $\lambda/2 = 0{\cdot}0003281$ mm.

Diminution of thickness of air layer, $\begin{cases} f'_2\lambda/2 = 0{\cdot}0099449, \\ f'_3\lambda/2 = 0{\cdot}0197720. \end{cases}$

Elongation of tripod screws = measured length of screws $\times$ ($a + 2bt$ for tripod alloy) $\times$ temperature interval,

$$l\left[10^{-9}\left(8600 + 4{\cdot}56\,\frac{t_1+t_2}{2}\right)\right](t_2 - t_1) = 0{\cdot}0064074,$$

$$l\left[10^{-9}\left(8600 + 4{\cdot}56\,\frac{t_1+t_3}{2}\right)\right](t_3 - t_1) = 0{\cdot}0125100.$$

Expansion of aluminium block = diminution of thickness of air layer + elongation of screws,

$$L_{t_2} - L_{t_1} = 0{\cdot}0099449 + 0{\cdot}0064074 = 0{\cdot}0163523.$$

$$L_{t_3} - L_{t_1} = 0{\cdot}019772 + 0{\cdot}012510 = 0{\cdot}032282.$$

$\theta = 0{\cdot}000\ 268\ 23.$ $\phi = 0{\cdot}000\ 000\ 125\ 31.$

$L_0 = 12{\cdot}1853.$

$a = 0{\cdot}000\ 022\ 013.$ $b = 0{\cdot}000\ 000\ 010\ 284.$

In order to form an idea of the kind of concordance afforded by determinations made on different days, the result obtained as above is compared below with the results of similar determinations made on two other days for slightly different temperature intervals :

a.	*b*.
0·000 022 013	0·000 000 010 284
22 070	10 617
22 041	10 895

The final mean accepted value for the expansion of aluminium is thus :

Mean coefficient $a + bt = 10^{-8}\ (2204 + 1{\cdot}06t)$, or

True coefficient $a + 2bt = 10^{-8}\ (2204 + 2{\cdot}12t)$.

It is not always possible to use the three-point method of contact in the case of crystals, for it frequently happens that crystals which are difficult to obtain of considerable size will be adequately long in the direction in which the expansion is to be determined, but narrower in other directions, so that the parallel-ended block will not stand on all three of any set of points. Also the aluminium disc with points below will not always stand on the upper end of the crystal, for a similar reason. In such cases the plane side of the platinum-iridium table is used, and a plane disc of aluminium is employed, and the crystal and disc are placed in position by sliding contact, to get rid of the air film. No appreciable difference has ever been observed by the author between the results in cases when this procedure has been followed and those obtained when three-point contact has occurred. This is probably owing to the perfection of planeness of the crystal surfaces produced by the cutting and grinding goniometer described in Chapter XLIII.

Another occasion when the plane side of the tripod table without points is used has already been referred to, namely, when the expansion of the platinum-iridium alloy is itself being determined. This is necessarily performed with the two reflecting surfaces concerned in the production of

the interference bands, the table top and the under surface of the glass wedge-disc, separated at a distance of somewhat over a centimetre. Either red cadmium or green mercury light requires to be used, as no other (unless it be that of neon) is sufficiently monochromatic to afford bands at so great a distance of separation of the surfaces, that is, no other radiation is sufficiently free from internal secondary interference. Moreover, the polish taken by platinum-iridium is so excellent that the reflection from the table top overpowers that from the glass wedge-disc ; but this difficulty is overcome by depositing on the lower relevant surface of the latter a thin film of silver by means of a silvering solution. The reflection from this surface is then enhanced, and at the same time less light reaches the platinum-iridium, so that the two reflections are now adequately equalised to afford black bands. In other respects the determination is carried out as described in the previous pages. The length of screws (mean of the three) employed in an actual determination was 12·369 millimetres, and this length was both L_{t_1} and d the thickness of the air layer. The initial temperature was 11·1°, corresponding to this length. This amount of screw produced in green mercury light 20·63 bands by its expansion, on raising the temperature to 68·5°, and 39·40 bands for the whole interval from 11·1° up to the higher limit 117·8°. The correction for alteration of the refraction of air was obviously unusually large, even the barometric pressure part being in this case quite serious ; the total corrections for the two intervals were +2·17 and +3·52 bands, bringing up the correct number of bands to 22·80 and 42·92. The particular value for the coefficient of expansion of platinum-iridium obtained from this determination was :

$$\alpha = a + 2bt = 10^{-9}\,(8588 + 4{\cdot}52t),$$

and the mean of five such determinations yielded the value which has been used in the calculations of the expansion of aluminium and of potassium sulphate quoted in the previous pages, namely,

$$\alpha = a + 2bt = 10^{-9}\,(8600 + 4{\cdot}56t) = 0{\cdot}000\ 008\ 600 + 0{\cdot}000\ 000\ 004\ 56t.$$

Cubical Expansion.—The thermal expansion was similarly determined along the axes b and c of a number of excellent large crystals of potassium sulphate, and the final results for the three axes are compared on the next page. Their sum is also taken, for, the directions being rectangular, this sum represents the coefficient of cubical expansion of potassium sulphate. For when the expression for the product of the expansions of the crystal in the three rectangular axial directions, which naturally gives the expansion of the solid, is examined, it is found to consist of a large number of terms of which the only ones that affect the fourth and last trustworthy place of significant figures in the coefficient of expansion for any temperature are the sums of the constants a and b respectively. If the crystal were of cubic symmetry, the expression for the cubical expansion would be three times the linear, that is, obtained by multiplying the constants a and b, as determined from the linear expansion, by three. For a tetragonal, hexagonal, or trigonal crystal the cubical expansion is obtained by adding to

the constants for the direction of the axis twice those for the direction perpendicular to the axis. In the case of a rhombic crystal such as potassium sulphate, in which the expansions along the three rectangular axial directions are unequal, the sum of the three different pairs of constants affords the cubical expansion. The same applies also to monoclinic and triclinic crystals.

Cubical Expansion of Potassium Sulphate.

		a.	*b*.
Linear expansion along axis	*a*	0·000 036 16	0·000 000 014 4
,, ,, ,,	*b*	0·000 032 25	0·000 000 014 1
,, ,, ,,	*c*	0·000 036 34	0·000 000 041 3
Cubical expansion of K_2SO_4 = sum =		0·000 104 75	0·000 000 069 8

Thus the mean coefficient of cubical expansion $a+bt$ of potassium sulphate between 0° and $t°$ is $0{\cdot}000\ 104\ 75+0{\cdot}000\ 000\ 069\ 8t$.

It may be interesting to quote the analogous results for the two other members of the eutropically isomorphous series, rubidium sulphate and cæsium sulphate. For convenience in comparison the values for all three salts are tabulated below.

Values of $\alpha=a+2bt$, the Cubical Coefficient of Expansion at any Temperature t, of Alkali Sulphates, or Mean Coefficient between any two Temperatures of which the Mean is t.

K_2SO_4	$0{\cdot}000\ 104\ 75+0{\cdot}000\ 000\ 139\ 6t$
Rb_2SO_4	$0{\cdot}000\ 103\ 14+0{\cdot}000\ 000\ 153\ 4t$
Cs_2SO_4	$0{\cdot}000\ 101\ 70+0{\cdot}000\ 000\ 162\ 0t$

It is interesting to observe that the values of each constant show a regular progression in the order of the atomic weights and atomic numbers of the three alkali metals. The values are very close together, showing how similarly, on the whole, analogously constituted chemical substances expand with rise of temperature. There is absolutely no doubt about the values, as the accuracy of the interference method is much greater than the difference between different salts.

As was pointed out on page 637 in Chapter XXXII. on density determinations, in which the cubical expansion of salts in general was required in order to correct density determinations by the Retgers immersion method to the standard temperature of 20°, chemical salts as a rule expand about 0·0001, that is, about one ten-thousandth of their bulk, for each degree centigrade of rise of temperature. For it is scarcely necessary to state that the real meaning of the above figures for the coefficient of expansion is, taking for example the case of potassium sulphate, that when unity represents the volume of the crystal at 0°, its volume at 1° C. would be 1·00010475; and that if, again, say, its volume at 10° were taken as unity, its volume at 11° would be $1{\cdot}00010475+0{\cdot}00000140=1{\cdot}00010615$. Similarly, if the volume were unity at 50°, at 51° it would be 1·00011173; and if unity at 100° it would be 1·00011871 at 101°. Hence, even at temperatures as high as 100°, the volume only increases one ten-thousandth on heating through one degree of temperature.

This chapter may fittingly conclude with a short list of coefficients of thermal expansion of some crystalline substances of the various systems of symmetry, as determined by Fizeau, by Benoit, employing Fizeau's apparatus, and by Reimerdes,with the dilatometer of Pulfrich. It must not be taken for granted that expansion is an invariable accompaniment of the rise of temperature of crystals, at any rate along every direction in the crystal. For a remarkable exception was discovered by Fizeau, in the case of hexagonal silver iodide, AgI, the thermal behaviour of that salt having been studied by him between the temperatures of $-10°$ and $+70°$ C. A crystal of silver iodide actually contracts along the hexagonal (crystallographic and optic) axis on warming, and this linear contraction increases as the temperature rises; moreover, so predominating is this contraction, as compared with the smaller expansion perpendicular to the axis (see figures in table), that the total volume of the crystal diminishes at an accelerating rate as its temperature rises. This contraction has been shown by other observers to continue until at the temperature of 146° silver iodide suddenly changes with absorption of heat into a cubic modification, and on cooling below this temperature passes back to the hexagonal variety. Hence, the greatest care must always be taken in employing the interference method, to verify that the alteration in length along the direction under observation is actually one of elongation. For the exceptional cases like silver iodide, and those also of calcite and beryl given in the table, will probably prove of the greatest value in the future in elucidating crystal structure.

Another curious phenomenon is that the diamond at $-41{\cdot}7°$, cuprite at $-4{\cdot}3°$, and beryl at $-4{\cdot}2°$, each reach a maximum density, at which the crystals begin to expand with further cooling. Hence, if the crystals were warmed from an original temperature lower than this limit they would resemble silver iodide in contracting with rise of temperature, until the limit was reached, after which they would commence to expand. It is noteworthy that the coefficients are very small in all three cases, that of cuprite being remarkably low.

Only one axis is identical with a crystallographic axis, the symmetry axis b, in the case of a monoclinic crystal, the other two axes of the thermal ellipsoid lying rectangularly in the symmetry plane. For gypsum, $CaSO_4 . 2H_2O$, the expansion along the symmetry axis was found by Fizeau to be

$$a = 0{\cdot}000\ 037\ 89, \qquad 2b = 0{\cdot}000\ 000\ 093\ 6;$$

and for the directions of the other two rectangular axes lying in the symmetry plane:

$$a = 0{\cdot}000\ 001\ 13, \qquad 2b = 0{\cdot}000\ 000\ 010\ 9, \text{ and}$$
$$a = 0{\cdot}000\ 027\ 96, \qquad 2b = 0{\cdot}000\ 000\ 034\ 3.$$

In order to obtain these values Fizeau[1] first prepared a cube of gypsum, of which one pair of faces was parallel to the symmetry plane, the expansion afforded along the direction perpendicular to this pair being obviously that for the direction of the symmetry axis b; the other

[1] *Comptes rendus*, 1868, *66*, 1005 and 1072; *Pogg. Ann.* 1868, *135*, 372.

two pairs of parallel faces possessed known orientations with respect to the crystallographic axes a and c. A fourth pair of parallel faces

VALUES OF α, COEFFICIENT OF LINEAR EXPANSION AT $t°$.

$\alpha = a + 2bt$.

System.	Substance.	Observer.	Direction.	a.	$2b$.
Cubic	Rock salt, NaCl	Fizeau	Any direction	0·000 038 59	0·000 000 044 9
,,	Fluorspar, CaF_2	,,	,,	017 96	028 8
,,	Pyrites, FeS_2	,,	,,	008 42	017 8
,,	Diamond, C	,,	,,	000 60	014 4
,,	Cuprite, Cu_2O	,,	,,	000 09	021 0
Tetragonal	Anatase, TiO_2	Fizeau	Par. axis	006 95	031 1
		,,	Perp. axis	003 50	029 5
Hexagonal	Silver iodide, AgI	Fizeau	Par. axis	−002 26	−042 7
		,,	Perp. axis	+000 10	+013 8
,,	Beryl, $Al_2Be_3(SiO_3)_6$	Fizeau	Par. axis	−001 52	011 4
		Benoit *	,,	−001 340	008 06
		Fizeau	Perp. axis	+000 84	013 3
		Benoit *	,,	000 994	009 30
Trigonal	Quartz, SiO_2	Fizeau	Par. axis	006 99	020 5
		Benoit *	,,	007 111	017 12
		Reimerdes †	,,	006 925	016 89
		Fizeau	Perp. axis	013 24	023 8
		Benoit *	,,	013 163	025 26
,,	Calcite, $CaCO_3$	Fizeau	Par. axis	025 57	016 0
		Benoit *	,,	024 963	027 34
		Fizeau	Perp. axis	−005 75	008 7
		Benoit *	,,	−005 541	001 94
,,	Sapphire, Al_2O_3	Fizeau	Par. axis	005 37	020 5
		,,	Perp. axis	004 53	022 5
Rhombic	Topaz, $(AlF)_2SiO_4$	Fizeau	Par. axis a	004 23	015 3
		,,	,, b	003 47	016 8
		,,	,, c	005 19	018 3
,,	Potassium sulphate, K_2SO_4	Tutton	Par. axis a	036 16	028 8
		,,	,, b	032 25	028 2
		,,	,, c	036 34	082 6
,,	Rubidium sulphate, Rb_2SO_4	Tutton	Par. axis a	036 37	040 6
		,,	,, b	032 14	036 8
		,,	,, c	034 63	076 0
,,	Cæsium sulphate, Cs_2SO_4	Tutton	Par. axis a	033 85	042 8
		,,	,, b	031 95	036 4
		,,	,, c	035 90	082 8

* Employing the apparatus of Fizeau. † Employing the apparatus of Pulfrich.

were then ground at two opposite corners of the cube. The expansion along the direction of the normal to each of the four pairs of faces then existing on the block was determined by this interference method. The

results were subsequently combined in four equations, from which it was possible to calculate the four unknown quantities, namely, the three linear expansions above given for the three axial directions of the thermal ellipsoid, and the angle of inclination of one of the two thermal axes lying in the symmetry plane with the inclined crystallographic axis *a*. This angle in the case of gypsum proved to be $+47° 44'$. The method is of general application for the determination of the coefficients of expansion of monoclinic crystals.

General Use of the Interferometer in Fine Measurement.—It has already been mentioned that the interferometer, as designed by the author for the measurement of the thermal expansion of crystals, is of general application for the measurement of very short distances or small amounts of motion, in terms (hundredths) of the half wave-length of any suitable truly homogeneous light radiation, monochromatic in the strictest sense. The half wave-length of the light is actually the visible gross unit of this refined scale, directly represented by any two adjacent interference bands, the distance between the centres of which, if red hydrogen light be employed, corresponds to a difference of thickness of the air-film between the two reflecting surfaces at the two positions occupied by the bands of 1/3048th of a millimetre or 1/77,419th of an inch. The micrometer eyepiece enables this grosser unit to be further subdivided into 100 parts, each of which may be read off directly on the drum, so that the fine unit of measurement directly indicated by the instrument is the 1/304,815th part of a millimetre or the 1/7,741,900th part of an inch, that is, in round numbers, the one eight-millionth of an inch. Another application of the interferometer will be dealt with in the next chapter, namely, in the measurement of the elasticity of crystals.

To convert the interferometer, which has been described in this chapter as part of the dilatometer, into its general form (in which form it will be employed in determining crystal elasticity), it is only necessary to remove the specifically thermal part of the apparatus, the interference chamber (*c* in Fig. 889, page 1309) of the dilatometer, by unscrewing it at *f* from the lower metallic end of the suspended partly porcelain tube *p*, and to substitute for it a simple brass cap to replace and serve the purpose of the roof-plate *d* of the interference chamber; the cap carries a similar screw thread to that at *f* of the latter, and also, in a similar rabbeted central aperture of one-inch opening, the glass refraction-countervailing wedge-disc *e* of 27 mm. diameter, tilted slightly by two little screws in the rabbet, in order to eliminate its reflections out of the way of the interfering reflections. The large glass cover-wedge (cut from the same glass plate-wedge of 35 minutes angle as the countervailing disc in the cap), the lower surface of which is to provide one of the interfering reflections, is in all cases to be carried by a little tripod, forming part of the specific apparatus which also carries the object, the movement of which is to be measured. The second plane surface furnishing the other of the two interfering reflections is to be either the moving surface of the object itself, or a black glass or aluminium surface moving rigidly with the object.

Demonstration and Experimentation Apparatus for the Interferometer.—A very useful apparatus is illustrated at D in Fig. 894, which has enabled the author to study the nature of the interference bands afforded by a great variety of sources of homogeneous light, with the aid of the interferometer in its perfectly general form A, B, C, which has just been described. A and B are the two separately mounted parts of the interferometer on their stout pedestals, and C is the cap carrying the countervailing

wedge-disc at the lower end of B. The demonstration apparatus D consists essentially of a hollow but rigid columnar support *a* for the interference tripod *b*, and within it a vertically movable (with exceedingly fine motion) shaft-support for the thick black glass disc, the finely polished absolutely truly plane upper surface of which is to act as the object-surface and to furnish the second reflection concerned in the interference. The pillar *a* rises from a heavy gun-metal cone *c* cast solid with the base-plate *d*, the latter being screwed down to the large plinth of hard mahogany on which the second part B of the interferometer is mounted. The interference tripod *b* rises from a stout split collar *e* gripping around the top of the pillar, and rigidly secured thereto by a tightening screw. The three little columns *b* of the tripod are hollow, and the cylindrical bore of

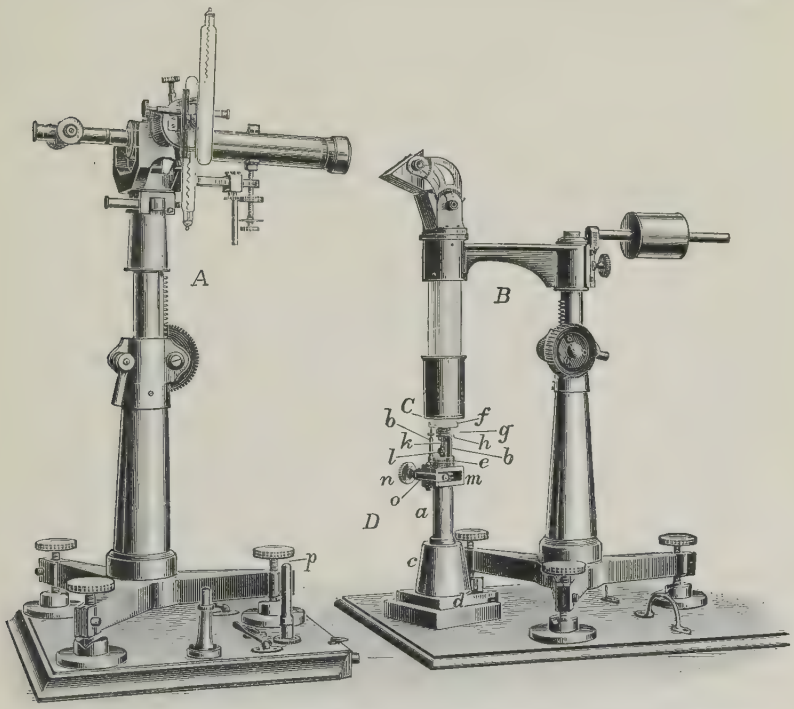


FIG. 894.—General Form of Interferometer A, B, C, in use with Experimental Interference Apparatus D.

each is tapped to engage with a screw of fine pitch and close fit, the upper termination of which is roundly pointed to act as one of three supports for the large glass interference wedge-disc *f*; the screw shaft expands some little distance below the summit into a milled head, for convenience in adjusting the height of the screw and therefore of the wedge-disc. The black glass disc is mounted by cement on the top of a metal disc *g*, and the latter is carried in an adjustable manner (by four screws) above a second metal disc *h*, rigidly carried at the head of the movable vertical column; the mode of attachment to the column provides for a considerable amount of rough vertical sliding adjustment, the disc being carried at the head of, and solid with, a hollow cylinder *k* about 3 centimetres in length, sliding up or down the top part of the column, and capable of rigid fixation at any position by means of a split collar and tightening screw *l* at its lower termination. Matters are so arranged that the upper (reflecting) surface of the black

glass head is brought to within a millimetre of the lower surface of the colourless glass wedge-plate lying on the tripod screws. The thickness of the air-film for maximum brightness of the interference bands in red C-hydrogen light is about $\frac{3}{4}$ mm. By the regulation of the tripod screws it is then readily possible to produce an ideally perfect field of interference bands, when the suspended tube of the part B of the interferometer is brought exactly over the centre of the tripod, so that the vertical axes of the suspended tube and the demonstration apparatus D form a continuous line, and assuming part A of the interferometer to be in position, as shown in Fig. 894, and the Geissler tube of hydrogen or neon to be in action with the aid of the induction coil.

The polished surface of the black glass head of the demonstration apparatus should have been once for all adjusted, with the aid of the little adjusting screws of the metal-disc supporting table, so that it is at right angles to the vertical axis of the apparatus—that is, truly horizontal—using a small spirit-level conveniently supplied for the purpose. It is also assumed that the inner vertical movable column carrying the black glass at its head is conveniently situated for use of the fine movement, with the very fine screw not far from the centre of its path. The construction of this fine vertical adjustment and the means of driving it, are as follows:

Just below the sliding coarse adjustment cylinder *k* of the black glass head the main vertical shaft thickens to 1·2 centimetres, and the whole of this thicker lower portion of the shaft slides readily but fairly tightly in the gun-metal column 2·8 centimetres diameter and 12 centimetres long, the flanged plinth of which is solid with the basal supporting cone. An exceedingly fine screw thread, one-fourth of a millimetre in pitch, has been cut on a part of the shaft within the column; rotation of the shaft is prevented by groove and pin, but it can be propelled upwards or downwards by a rotatable but vertically immovable driving wheel, furnished with a correspondingly fine screw thread within and 72 oblique worm-wheel teeth without. The fixed outer column is broken to admit the wheel at a point 2·2 centimetres from the top, but the two parts are rigidly united and a suitable support afforded for the bearings of a driving endless-screw, by a hollow rectangular box-piece *m*, open in front and behind, cast solid with the two parts of the column. One revolution of the endless-screw, by means of a large milled head *n* provided, rotates the wheel to the extent of one tooth, which corresponds to a movement of the vertical shaft and its black glass head of 0·0035 millimetre. The bearings of the endless-screw are attached to the box by an enveloping double claw *o*, cast in one piece and adjustable as regards the pressure between screw and worm-wheel, and the shaft of the screw which emerges from the front bearing is notched to take the correspondingly pinned hollow attaching (axial) cylinder of either the simple milled head *n* referred to and shown in the figure, or of a similar milled head at the end of a much longer driving shaft, which brings the head conveniently much nearer to the observer at the eyepiece of the interferometer (part A). When this arrangement is used, the whole demonstration apparatus D is rotated about 90° anti-clockwise, from the position shown in the figure. To support the near end of this longer driving axle a little cylindrical bearing column is supplied, which, being hollow, can be adjusted for height by fitting fairly tightly over a solid pillar *p* of circular section, firmly fixed to the mahogany base-board of A by screws passing through a flanged base in which the lower end of the little column terminates; the hollow column carries at its summit an adjustable (rotatable) ring-bearing for the axle, and its adjustment for height and rotation enables the long driving axle to be arranged truly horizontally and for the minimum of friction in the ring-bearing.

When the interference bands have been adjusted as already described above, exactly as shown in Fig. 891, the slightest rotation of the milled head *n* of the endless-screw (or that of the long driving rod) alters infinitesimally the thickness of the air-film between the black and colourless glass surfaces, and causes the interference bands to move parallel to themselves with complete steadiness, past the reference centre (the centre of the miniature silver ring at the centre of the lower reflecting surface of the

colourless glass wedge-plate, shown in Fig. 891) and the pair of vertical spider-lines which should have been adjusted symmetrically about the centre of the little ring, as in the measurements of thermal dilatation.

This demonstration apparatus has proved most useful. In a second model which the author has had constructed, the coarse vertical movement of the black glass head has been given a rack and pinion adjustment, instead of merely one by hand-sliding; also the movement is supplied with a fine scale and vernier on silver, reading directly to half-millimetres and with the aid of the vernier to the fiftieth of a millimetre, 0·02 mm. By this means a careful preliminary adjustment of the two reflecting surfaces can be effected to any desired thickness of the air-film between them, and experiments on suitable thicknesses for specific radiations more readily carried out.

CHAPTER LVIII

ELASTICITY OF CRYSTALS AND ITS INTERFEROMETRIC MEASUREMENT—THE ELASMOMETER AND TORSOMETER—MICHELSON'S AND FABRY AND PEROT'S INTERFEROMETERS—INTERFERENCE FRINGES IN MICA

CRYSTALS exhibit their orientated structure very clearly in the different elasticity, or resistance to temporary deformation, which they show in different directions. The attempted deformation may obviously be of two kinds: (1) of compression such as that by a weight placed on (above) the crystal, which may conveniently be an elongated prism resting by one of its plane ends (cut or a natural face perpendicular to its upright length) on a relatively immovable support, and (2) of extension such as that effected by means of a weight suspended from the lower end of (below) the crystal, while the latter is fixed at its upper end. The amount of deformation, whether compression or dilatation, will clearly depend on the force employed and on the dimensions of the crystal. But a third factor also enters into the case, namely, the specific power of the crystal to resist such deformation, a power which in turn depends both on the nature of the substance and on the symmetry of its structure. This specific resistance to change of form is known in mechanics for non-crystallised substances, or substances such as metals which, although crystalline, are composed of a mass of interlacing anyhow-orientated crystals, and so produce an average effect, as the **"Modulus of Elasticity,"** and is distinguished by the letter E. It was so named by Dr. Thomas Young, and hence it is commonly called "Young's Modulus."[1]

Let us suppose we are dealing simply with a vertical wire, of length L and sectional area Q, attached at the top to a rigid support, and stretched by a weight just adequate to keep it taut; if we then add another weight P at the lower end, the wire will stretch further by an amount l, and the modulus of elasticity E corresponding to the stretching is, according to Kohlrausch:

$$E = \frac{L}{l} \cdot \frac{P}{Q}.$$

[1] The Modulus of Elasticity E is termed in German nomenclature (*e.g.* by von Groth, Liebisch, and Voigt) the "Dehnungswiderstand" (resistance to extension). Its reciprocal, $\frac{1}{E}$ of our nomenclature, is unfortunately called E by the German authors, and named the "Dehnungskoeffizient" (extension coefficient). This fact requires to be carefully noted, as confusion is otherwise likely to occur.

We can define the modulus of elasticity as **that weight in kilograms which must be hung on a wire of one square millimetre section in order to double its length,** supposing the elongation to be proportional to the load. For if Q = 1 and l = L we have E = P.

The modulus of elasticity E, the coefficient of resistance to dilatation or bending, is usually determined by observations of the bending of a rod when loaded with a given weight. The simplest manner is to clamp the rod, horizontally arranged, and of free length L, at one end, the free end pointing to a scale; to load this free end with a weight of P grammes, and to observe the deflection s produced. If the rod be of rectangular section with vertical side or thickness t and horizontal side or breadth b, then E is afforded by the formula of Kohlrausch:

$$E = 4\frac{P}{s} \cdot \frac{L^3}{t^3 b}.$$

A much better method of procedure, however, and the one currently employed, which avoids all the uncertainty introduced by the clamping of the rod, is to lay it with both ends loose upon the parallel edges of two wedge-shaped supports, as shown in Fig. 895. Here L represents the distance between the two supports, that is, the free length of the rod, and the weight P is suspended from the middle of the rod, generally from a wedge-stirrup, producing a deflection there of s. The Kohlrausch formula then becomes:

FIG. 895.

$$E = \frac{1}{4} \cdot \frac{P}{s} \cdot \frac{L^3}{t^3 b}.$$

If the rod be of circular section, of radius r, the $t^3 b$ of the denominator is replaced by $3\pi r^4$ in both the above formulæ.

All lengths are conveniently expressed in millimetres and the weights in grammes, so that the result shall be expressed in terms of the currently accepted unit of the modulus of elasticity.

There are three obvious assumptions made, in order that the formula may correctly express the facts, namely, that the deflection s produced by P is small in comparison with L, that the load used is far from the breaking strain, and that the substance is a truly elastic one, not suffering any appreciable permanent deflection as the result of the operations.

In the year 1878 Warburg and Koch[1] showed that the above formula of Kohlrausch affords only a first approximation, and that the experimental facts are better interpreted when a second term is introduced, namely, the product of the Kohlrausch formula with $3\left(\frac{t}{L}\right)^2$, the whole formula being then:

$$E = \frac{1}{4} \cdot \frac{P}{s} \cdot \frac{L^3}{t^3 b}\left\{1 + 3\left(\frac{t}{L}\right)^2\right\}.$$

[1] *Ann. der Phys. und Chem.*, 1878, *5*, 253.

For most substances the second term proves to be far from negligible, when the determinations are carried out with good crystals or a homogeneous rod of whatever material is under observation, and with the accuracy possible to the interference method introduced by Koch in the same memoir. The method formerly used was the mechanical one of Neumann, as improved by Voigt, to whom we owe most of the work on the elasticity of crystals which has yet been carried out. It is simply the ordinary mechanical laboratory method above referred to carried to extreme refinement, with crystal plates or rods as large as are procurable. The interference method of Koch was based on the same principle as that underlying the Fizeau dilatometer explained in the last chapter, as regards the mode of measuring the bending, sodium light being used. The plate was laid on the edges of two sloping blocks, and a bending weight applied above its centre, either through a point at the end of a hook, or by a stirrup knife-edge. The lower surface of the plate, and the upper surface of a totally reflecting prism supported very closely beneath it, with only a thin film of air intervening, were the two surfaces affording the interfering reflections producing the interference fringes. A complicated and somewhat cumbersome method was adopted for suspending the weight from the hook or stirrup, and for regulating and graduating the application of the load. The excellent results obtained for the thermal expansion of crystals with the author's interferometer-dilatometer described in the last chapter, and the desirability of improving Koch's apparatus as regards the mode of application and control of the weight, caused the author[1] to devise an interference elasticity apparatus involving the use of the interferometer part of the dilatometer, in its general form as stated on page 1330 and illustrated in Fig. 894, combined with a much more refined and accurate arrangement for applying and controlling the load. The whole apparatus, as arranged for the purpose of the determination of bending, has been termed the "elasmometer," and is described in the next section but one (page 1339) and illustrated in Fig. 897.

Variation of Elasticity with Symmetry.—When the elasticity E, the resistance to deformation, is thus determined along different directions in a non-crystalline substance such as glass, or in a crystalline substance composed of small individual crystals interlaced in a mass with every possible orientation, such as cast iron, the values found for the various directions are all equal within the limits of the possible experimental error. Hence for such a substance E has only one value, **the** modulus of elasticity.

In the case of a crystal, however, the value varies in general for different directions, and in a manner which is compatible with the degree of symmetry exhibited by the crystal. Moreover, this variation of the modulus of elasticity affects all regular vibratory movements transmitted through a crystal, such as sound waves, the velocity of which is proportional to the square root of the modulus of elasticity and inversely proportional to the square root of the density, that is,

[1] *Phil. Trans.*, 1904, A, *202*, 143.

proportional to $\sqrt{\frac{E}{d}}$. This has been proved by Savart for sound travelling through quartz, plates of which set in vibration give different dust figures according to their orientation in the crystal, and by von Groth for rock salt by direct measurement of the velocity of sound in the crystal.

In order to be able to specify the modulus of elasticity E for **any** direction in a crystal, and thus to arrive at the surface of elasticity, the envelope on which lie the ends of all the radiating straight lines drawn from a given point to represent the elasticity, it is not sufficient, in the present state of our knowledge, to determine only the resistance to bending with a number of plates cut in different directions out of the crystal, but in addition we have to determine another factor, the resistance to torsion, F. The experimental determination of the torsion coefficient of a solid is carried out by supporting it firmly at one end while a twist is given to it at the other end, the force acting in the plane of the cross-section. The experiment, however, is clearly not one that can be easily carried out with a rod of an object so small as a crystal—even the maximum one that can be grown—often is, and the methods at present used are all mechanical and require a large-sized crystal. That of Voigt[1] is the best of these, which is comparable to the mechanical method of Neumann, as also improved by Voigt, for the determination of the bending. The torsion apparatus of Voigt will presently be described.

The author has arranged, however, to extend the interference method to the determination of the torsion coefficients of crystals, an apparatus for the purpose being now under construction (its completion having been delayed by the War); for the accuracy of the mechanical method can never hope to approach anywhere near that now attained in the determination of bending by the interference method.

The work of Neumann and especially of Voigt has shown that for the complete expression of the elasticity relations in different directions of a triclinic crystal, the general case, no less than 21 elasticity constants are required (that is, occur in the general equation expressing E directionally), which reduce in stages, by some of these constants becoming identical, as symmetry is introduced. For a monoclinic crystal there are 13, for a rhombic crystal 9, for a hexagonal crystal these reduce to 7, and still further to 6 for a tetragonal crystal, while finally for a cubic crystal there are only 3 elasticity constants. By determinations of bending alone, however numerous and varied in direction, at most 15 of the 21 can be calculated. But when both bending and torsion determinations are available for several differently orientated plates or bars, the whole of these constants can be more or less readily calculated. The surface of elasticity is a sphere for substances which are either not crystalline, or are composed of interlacing crystals having every possible orientation, so that the substances behave as if amorphous. For a crystal, even a cubic one, the surface is no longer spherical, but is centro-symmetrical at least, the two parts of every diameter passing through the central point chosen (from which

[1] *Ann. der Phys.*, N.F., 1886, *29*, 604; 1887, *31*, 721; 1888, *35*, 642. See also Liebisch's *Physikalische Krystallographie*, Fig. 290, page 562.

lines representative of the elasticity are drawn) being equal. The shape of this surface is not an ellipsoid, like the general surface of optical vibration velocity, of refractive index, or of thermal deformation, but is merely conditioned by the fact that every direction of equal value in regard to the morphological symmetry has an elasticity diameter of equal length.

In the case of a cubic crystal the surface is one characterised by the three constants above referred to; the three rectangular cubic (tetragonal) axes are equal axes of maximum or minimum elasticity, the four trigonal axes joining the corners of the cube and equally inclined to the cubic axes are the converse, the directions either of the minimum or maximum elasticity, while the six digonal axes of symmetry bisecting the angles of the cubic axes and proceeding from the middle of the edges are axes of intermediate elasticity. Thus Fig. 896 represents the elasticity surface of iron pyrites according to the German nomenclature (see footnote on page 1334). The radii vectores are expressed in terms of the German E, the "Dehnungskoeffizient," the reciprocal $\frac{1}{E}$ of our Young's modulus E. Here the cubic axes *c* are the minima, while the trigonal axes *o* normal to the octahedron faces are the maxima of elasticity of the whole crystal. The digonal axes *d* normal to the rhombic dodecahedron faces are for this crystal greater than *c* but less than *o*. Sections of the elasticity surface parallel to the faces of the octahedron are circular. Fluorspar and rock salt exhibit similar surfaces, while the alums, the cubic double sulphates of the series $R_2SO_4 . M_2(SO_4)_3 . 24H_2O$, are characterised by elasticity surfaces which have protuberances instead of depressions and *vice versa*. The figures representing Young's modulus, however, would resemble Fig. 896 in the case of the alums.

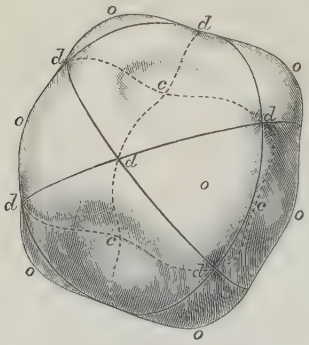


FIG. 896.—Elasticity Surface of Iron Pyrites.

Crystals belonging to the other systems of symmetry exhibit analogous surfaces of elasticity, characterised by the symmetry of the particular system, that is, they possess the same planes of symmetry as the crystal itself.

Thus the property of elasticity, like the optical and thermal properties and that of hardness, is a function of the symmetry, and we have in this fact the final expression of the fundamental importance of symmetry of internal structure, as the dominant fact of crystallography, causing and governing not only symmetry of exterior form, the most obvious of all the properties of crystals, but also the symmetrical display of every physical property.

The description of the author's elasmometer will now be given, and of the method of determining bending with its aid, including an actual example, that of iron pyrites. This will be followed by a description, as far as is yet possible, of the interference torsion apparatus, the "torsometer," now under construction for the author, and an account of its contemplated mode of use.

The Measurement of s, the Bending at the Centre of an elongated Plate supported near both Ends, by the Elasmometer.—The optical portion of

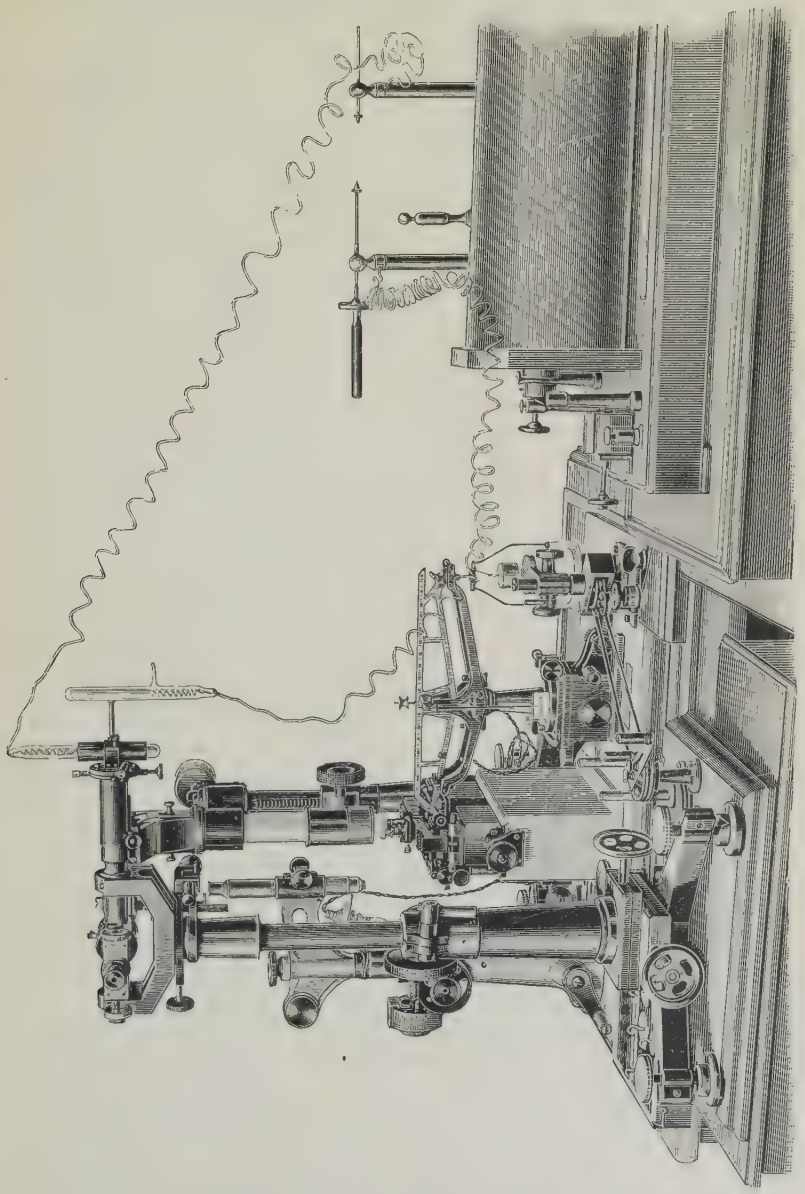


FIG. 897.—The Elasmometer, with Interferometer in Action, employing Red Hydrogen Light.

the apparatus consists of the author's interferometer, exactly as described in the last chapter, in connection with the dilatometer, and in the later

section (page 1330) on the general form of the interferometer. It is shown in position in Fig. 897, and the elasmometer proper by itself in Fig. 898.

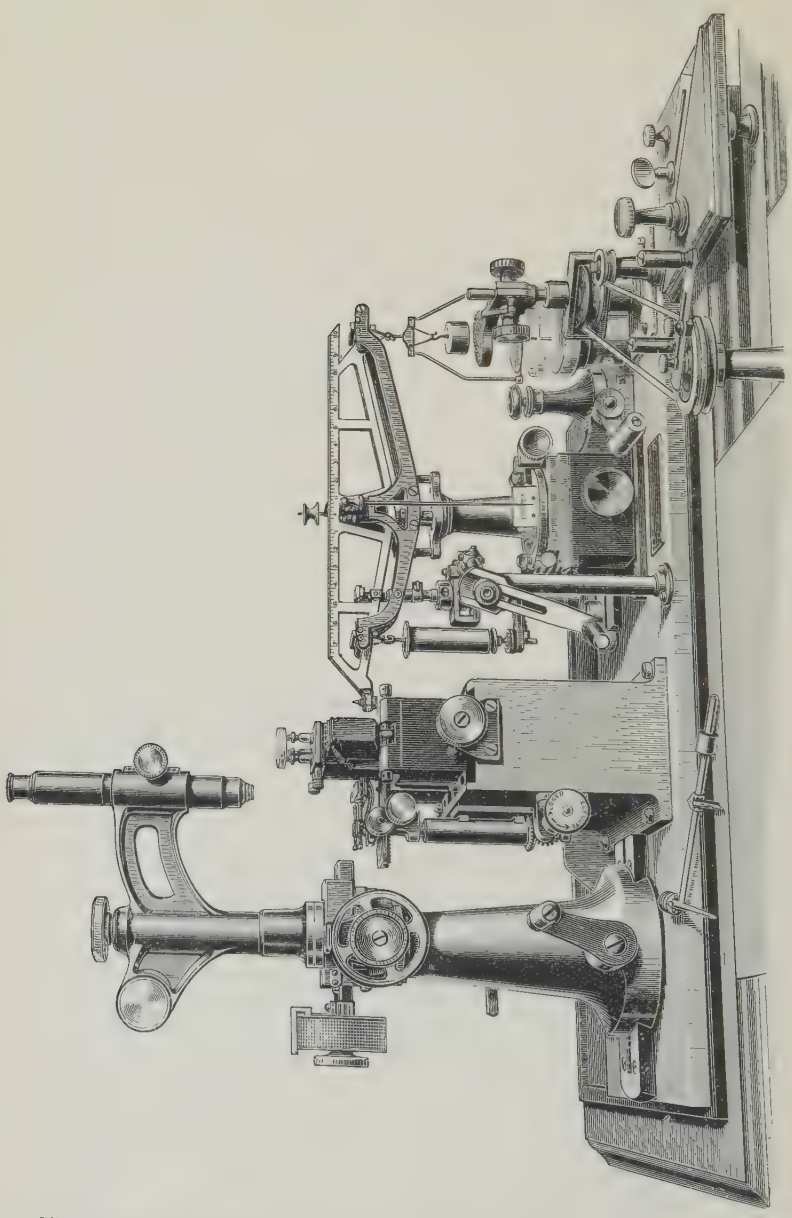


Fig. 898.—The Elasmometer Proper.

The auto-collimating telescope pedestal stands on a small plinth attachable in front to the main plinth of the elasmometer proper. The

second pedestal of the interferometer, carrying the refracting prisms and the partially porcelain suspended tube, is mounted on three toe-plates, ready fixed for the reception of its levelling screws, on the back part of the metal base of the elasmometer proper. The lower end of the suspended tube carries a simple cap, as described on page 1330, with a circular aperture of one inch diameter, in which is mounted slightly obliquely the countervailing wedge-disc (*e* in Fig. 889, p. 1309) of the interference apparatus referred to on page 1313. This cap replaces the interference chamber of the dilatometer, the rest of the interference apparatus being carried by the elasmometer proper, immediately under the cap when the suspended tube is swung into position, as described on page 1332 for the general mode of use of the interferometer.

The **Elasmometer** proper consists of seven essential parts, which will be briefly described in turn.

(1) **A pair of platinum-iridium wedges** are arranged parallel to each other, and with their knife-edges downwards (the method of Fig. 895 being inverted), up against which the plate (usually an elongated one) of the crystal or other substance under investigation is to be bent, by a weight applied under its centre by means of an upright agate point carried at the end of a balance beam, as shown in Fig. 899. They are carried by a pair of gun-metal blocks arranged in the same straight line, and underneath overhanging portions of the blocks ; the latter approach each other, thus forming a commodious recess, and the blocks and therefore the wedges are adjustable for their distance apart. This recess formed underneath these overhanging parts of the blocks accommodates the plate-supporting apparatus and the weight-applying end of the balance, both of which can be independently moved either into or out of the recess at will. These gun-metal blocks slide on a large rigid block of steel, mounted to the front and left of the centre of the iron base, and the front block is provided with fine adjustments for altitude and azimuth, to enable the parallelism of the wedges to be accurately attained.

(2) **The interference tripod**, consisting of three adjustable capstan screws, for supporting the large colourless glass wedge-disc, the under surface of which is the upper one of the two surfaces which are to reflect the interfering light, is carried by the gun-metal blocks, two of its screws being supported on the front block and the third on the one behind. The pair of screws and the single screw are in each case directly mounted on a small but thick plate with wide dovetailed groove, sliding over a corresponding dovetail fixed to the block, in order that the separation of the two front screws from the back screw may be adjusted to suit the size of glass wedge-disc employed.

(3) **A transmitter of the bending motion** of the centre of the plate to the interference apparatus, and itself furnishing the second (lower) of the two essential reflecting surfaces of the latter, is fitted between the two inner closely approached ends of the blocks. It is best shown in Fig. 899 (being removed in Fig. 898), and consists of a vertical rod of aluminium, resting by its roundly pointed lower end on the centre of the crystal plate, and carrying a head-piece above terminating in an adjustable horizontal black-glass disc, the truly plane polished upper surface of which is the reflecting surface just alluded to, relevant to the interference. The upper portion of the rod is of fluted square section, in order to slide without friction in a square vertical boring in an arm screwed with slot adjustment to the front block, between the two tripod screws.

An alternative form of transmitter with similar black-glass head is seen lying on the left front of the base in Fig. 898 ; it is a nearly counterbalanced rocker, having a

fulcrum knife-edge of agate, intended to rest on an agate plate carried on the front block, to the left in Fig. 899. Usually the first form of transmitter is much preferable.

(4) **A pair of mechanical fingers**, shown in Fig. 900, are provided for preliminarily adjusting the crystal-plate and supporting it up against the platinum-iridium wedges until the pressure point of the balance is brought into action under the centre of the plate. They are carried to the left of the steel block in such an adjustable manner that they may be racked into or out of the recess by means of the large milled head shown below in Fig. 900, and raised or lowered by the still larger milled head seen below the column in Fig. 898. The two "Fingers" terminate in spring tables, each having a knife-edge as shown separately to the right in Fig. 900, and which are capable of adjustment for their distance apart parallel to the plate by the middle milled-headed screw in Fig. 900, which is right- and left-handed in its two parts

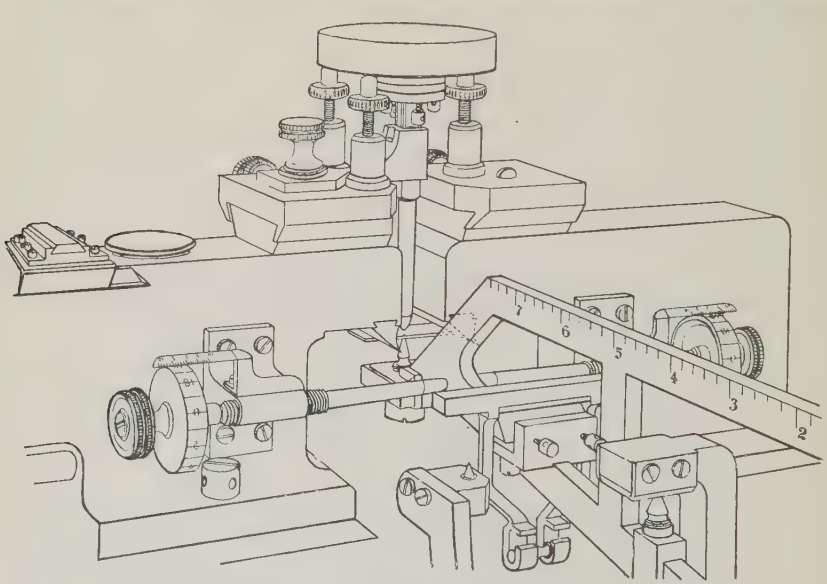


FIG. 899.—The Platinum-iridium Wedges, Crystal-plate, Balance and its Pressure Point, and Interference Apparatus of the Elasmometer.

moving respectively the two knife-edges. The plate is laid over the latter, and its position thereon may be delicately adjusted by two pairs of screws parallel to and perpendicular to its length, in a manner which will be clear from the figure.

(5) **A balance for the delivery of the load**, specially constructed by Oertling, is arranged to the right of the steel block. It carries at the left end instead of a pan the "pressure point," an upright agate cone, which is covered with a soft kid-leather cone during the experiment in order to protect the crystal from scratching. The bending weight is applied through this cone, and is equal to the weight placed in the pan at the right end. The whole balance is movable in the direction of its length, like the mechanical fingers on the other side of the steel block, so as to be able to bring the pressure point in or out of the recess, by means of a basal rack and a pinion provided with handle. A fine adjustment for azimuth is also provided, by means of the screw seen approaching the observer on the right at the top of the basal box on which the balance stands. These two movements thus enable the pressure point to be accurately centred under the crystal-plate. In order to avoid frequent repetition of this centring,

during a series of observations with the same plate, a pair of fine horizontal adjusting screws with ivory tips and divided drumheads are arranged, one on each side of the beam near the pressure point. They are carried by the blocks on their right side, and are well shown in Fig. 899. The ivory tips are arranged just to touch the beam when the centring has been accomplished, and the readings of the drums are noted for these adjusted positions ; they are then withdrawn for a noted number of turns, say one or two, of the screws during an observation, and reinstated before the next observation in order to ensure the continued adjustment of the pressure point, and withdrawn again before the observation is carried out.

The aluminium pan at the right end is connected by a central vertical rod with a second lower pan, a plane disc of aluminium, which is immersed during the observations in a dish of cedar oil, and the function of which is so to steady the balance during the application of the weight as to prevent absolutely all flickering of the

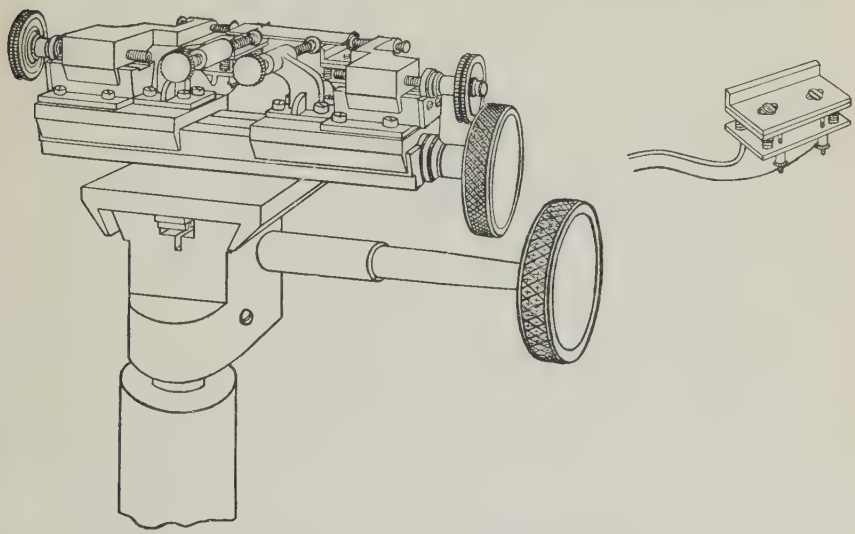


FIG. 900.—Mechanical Fingers for adjusting the Crystal-plate.

interference bands, which is otherwise a serious difficulty. A cylindrical counterpoise for the pan and aluminium steadier is suspended on the left side by the usual stirrup and agate wedge and plate. Weights up to 500 grammes may be employed as the load, and the sensibility of the balance up to this load is scarcely affected by the cedar oil immersion of the aluminium disc.

(6) **A control apparatus** is provided for the application of the load. If the weight were laid directly on the pan—when the pressure point has been adjusted under the centre of the crystal-plate—the bending would occur at once as soon as the balance were set in motion, by lowering the usual rests with the aid of the large milled head in front of the basal box, and the interference bands would flash past far too rapidly to enable them to be counted. Each of the platinised and carefully standardised weights, therefore, is provided with a hook instead of a knob, for suspension in a loop of soft but strong string carried by and below the suspension bar of the pan fitting. The weight is laid on a stout little circular table adjustable for height just below the string loop, covered with broadcloth and forming the flat expanded end of an arm proceeding from a slider about a stout column. This coarse vertical motion is by rack and pinion, manipulated

by either of the two milled heads seen in Figs. 897 and 898 to right and left of the column; fixation at any height can be accomplished by a clamping screw with lever head. The column itself is cylindrical and is susceptible of a very fine slow vertical motion, without rotation, in a correspondingly cylindrical keyed boring in a basal casting, which provides at the same time a rectangular box-like expansion, open at two opposite sides, for the driving-nut wheel of the screw tapped on the lower part of the column. The screw and nut are of quarter-millimetre pitch, so that a very fine motion is achieved, either by manipulation of the driving-nut itself, or more conveniently by means of the pulley wheel seen in front in Figs. 897 and 898, which is provided with a radial arm and handle for greater radius of rotation. The band is kept taut by a third pulley pressed in from the right by the little attachment seen to the extreme right in Figs. 897 and 898.

With the aid of the coarse adjustment the weight table can be lowered until the hook of the weight just touches and all but rests in the string loop. The fine movement of the table is then resorted to and the weight brought extremely slowly into action, the retardation being assisted by the regularly growing tension on the string, until the full weight is eventually operative. So perfect is this control, that the interference bands may be made to pass the reference spot in the centre of the field with any desired degree of slowness, or each band may even be held at the centre for an indefinite length of time. The counting of the bands is, therefore, a perfectly easy matter.

A further possible control, for the movement of the balance beam and pressure point, is provided in case of need in the form of an exceedingly fine vertical movement of an agate plate above, and intended to press against, an agate wedge on the beam between the fulcrum and the counterpoise. The agate plate is carried under the hook-shaped head of a vertical column, which is capable of a similar very fine motion in an outer column to that provided in the experimental apparatus D described and illustrated on page 1331; the hook head is also capable of coarse adjustment for height in the same way as the black-glass head of that apparatus. This control can be removed if not needed, and latterly the author has used the string loop control entirely by preference. It is adequate to remove the hook head.

(7) **A measuring microscope** is also provided, wherewith to determine *in situ* the dimensions of the crystal-plate and to find its centre. It stands to the left of the apparatus, and is best shown in Fig. 898. Each of its two rectangular measuring movements reads directly on the single screw itself (of millimetre pitch) to the thousandth of a millimetre, the head being provided with a large silvered drum divided into 100 parts directly; the tenths of these are obtained by engraving ten other circles on the cylinder of the drum, parallel to the divided edge-circle and equidistant from each other, and oblique lines from every division of the edge-circle (the first) to the next division on the other edge-circle (the eleventh). The tenth-part of a division of the edge-circle is then read off by means of an indicator-line on a glass plate carried in a frame above the drum, the centre of the glass being engraved with a single line coloured red parallel to the screw axis, the reading being afforded by the coincidence of the red line with the nearest intersection of an oblique line with a circle. Each screw is provided with a special device to prevent backlash, so that the readings afforded in this manner by a single screw, in the case of each of the two rectangular movements, are most accurate and very easy to take.

The conical column supporting the microscope is mounted on the top of the upper measuring movement, and the outer cone, from an arm of which the microscope is suspended, is capable of rotation about this inner cone, so that the microscope may be turned out of the way after it has served its purpose, and replaced over the interference apparatus by the interferometer suspended tube. A fixing screw is provided at the summit of the cone, and the microscope is counterbalanced on the other side of the column. The lower measuring movement is mounted in an adjustable manner, and

made rigid after the adjustment, on a stout pedestal movable, in the direction of the length of the elasmometer, over a bevelled guiding bed by rack and pinion, the latter provided with the handle seen in front. The two-thirds of a rotation possible to the handle are adequate to bring the microscope over the interference apparatus or remove it well out of the way, when more room is required than is obtained by merely rotating the upper part carrying the microscope. A clamping lever is just seen emerging behind the pedestal, for fixing the microscope rigidly during measuring operations.

The Determination of Bending is carried out in the following manner by means of the elasmometer. The plate of the crystal or other substance the elasticity of which is to be determined, and the thickness of which has been measured on a thickness measurer such as that shown in Fig. 893 (page 1320), is laid temporarily on the gun-metal knife-edges of the mechanical fingers, and its length and breadth measured with the aid of the measuring microscope. It is then adjusted to the platinum-iridium knife-edges by means of the various movements and adjusting screws of the mechanical fingers. The pressure-point is then adjusted below the plate centre, while the balance is out of action in its rests. The transmitter is next placed in position above the centre. A small preponderance of weight is then given to the pan side of the balance, in order that when the latter is released, which may now occur, the pressure-point may press up against the centre, with just enough weight to keep the plate in full contact with the platinum-iridium knife-edges, when the gun-metal ones are lowered and withdrawn.

The operation of bending the plate is thus always started with a small constant weight in action, and the plate very slightly preliminarily bent. It is the effect of the additional weights subsequently added from the control apparatus, in producing movement of the interference bands corresponding to further bending of the plate, that is to be measured. This small preliminary weight is effectively given to the pan end of the balance by merely removing the cylindrical counterpoise from the left side ; the weight of this is about 83 grammes, which, when the relative positions on the two arms of the balance are taken into account, is equivalent to a weight of 60 grammes on the pan, an amount of the right order to ensure effective contact of the plate with the platinum-iridium knife-edges.

The interference apparatus is next adjusted, if any further slight adjustment be necessary after the preliminary setting or a previous observation, to give an excellent field of vertical bands (as shown in Fig. 891, p. 1311) as seen through the telescope. The position of the bands is then measured in order to determine the initial fraction of a band, in the event of a band not being already centred on the silver ring and between the vertical pair of spider-lines.

The weight, the bending effect of which is to be measured, is then placed on the control table, and the latter lowered by the quick movement until its hook nearly touches the string loop. An eye must then be given to the interference bands, and the right hand used to continue the lowering of the weight with the utmost gentleness by one of the milled heads of the coarse movement, until the hook touches the string ; this can easily be done so gently that only a single band moves parallel to itself very

slowly past the reference centre of the silvered ring, as the tension on the string gradually increases. Recourse must then be had to the fine movement, and the driving wheel of the latter slowly rotated by means of the long lever handle, in the direction which is known by experience to lower the weight. The bands will immediately recommence their movement and pass one by one as the wheel is rotated, so steadily in fact, that each band can be held over the reference centre as long as may be desired, and the counting is exceedingly easy. Their movement is very slow at first as the tension on the string is increasing, but they go somewhat more quickly as the loop tightens, slackening again, however, towards the finish, until eventually the weight is left altogether suspended in the loop and quite clear of the table, when the bands also come completely to rest. No trembling of the bands is perceived, owing to the resistance of the aluminium disc immersed in the dish of cedar oil. Moreover, the bands can be recounted as the weight is again taken up by the table and as slowly removed from the loop by the reverse motion of the driving wheel. The bands repass equally steadily and deliberately.

When the weight is in full operation, and the bands are at rest, the last fraction is measured with the micrometer just like the first fraction, and the two fractions are added to the whole number of traversed bands, in order to arrive at the total corresponding to the bending. Similarly, on arriving back at the starting-point, with the weight entirely removed, the position of the bands is again measured for any fraction, which should be the same as at first. The operations can be repeated as often as desired, the lateral screws for the fine adjustment of the pressure-point being employed between each pair of determinations, and then again withdrawn. After the completion of the determinations for the first load, another greater weight is used, and a set of observations taken for it, and so on for as many different loads as one wishes to employ. The loads generally employed by the author are 100, 200, 300, and 400 grammes, and occasionally, if the plate will stand it, 500 grammes, the limit of the instrument.

The most convenient dimensions of the plate of the crystal or other substance investigated are about a couple of centimetres in length, a thickness of a millimetre or less, and a width not greater than half the length.

This description may conclude with an example taken from a series of observations made with four plates 2 cm. long of an excellent cubic crystal of iron pyrites, FeS_2, from Cornwall. Each plate was cut by Messrs. Hilger truly parallel to a face of the cube, and with its edge-faces parallel to the two other rectangular facial planes of the cube. Similar sets of plates of fluorspar and rock salt have also been cut and polished by Messrs. Hilger, for use in determinations of bending with the elasmometer, which it is hoped to carry out shortly. The length (between the wedges) of the plate of pyrites serving as our example was 17·261 mm., its breadth was 8·833 mm., and its thickness 0·875 mm. The number of interference bands in red hydrogen light which were caused to effect their transit for successive loads of 100, 200, 300, and 400 grammes are given on the next page, together with the differences for each increment of 100 grammes,

and their mean. Plate No. 1 broke under a load of 500 grammes, so that 400 grammes is the safe limit of weight the plates will withstand. The observations were made on four different days, with at least four days' interval, in order to permit recovery from any slight strain. Red C-hydrogen light was employed as source of light, the half wave-length of which is 0·0003281 mm.

The actual distance s through which the centre of the plate was bent for a load increment P of 100 grammes was :

$$s = 2 \cdot 27 \times \lambda/2 = 2 \cdot 27 \times 0 \cdot 0003281 = 0 \cdot 0007448 \text{ millimetre.}$$

Plate 2 of Pyrites.

Corrected No. of Bands for load of				Difference in No. of Bands for loads of			Mean difference for 100 grammes additional load.
100 gr.	200 gr.	300 gr.	400 gr.	100 and 200.	200 and 300.	300 and 400.	
2·14	4·44	6·66	8·99	2·30	2·22	2·33	2·28
2·30	4·54	6·76	9·02	2·24	2·22	2·26	2·24
2·16	4·45	6·69	8·98	2·29	2·24	2·29	2·27
2·27	4·52	6·82	9·17	2·25	2·30	2·35	2·30

Final mean corrected number of bands passing for increment of 100 grammes 2·27.

The above results are observed to be satisfactorily concordant, notwithstanding the fact that the number of bands passing per 100 grammes of load is so small with pyrites, on account of the extreme resistance to bending exhibited exceptionally by this mineral. With most other substances very many more bands would pass for the same amount of load and size of plate. Perhaps the best indication of trustworthiness of the method is the closeness of the numbers of bands in the four experiments for the highest load of 400 grammes (maximum difference 2 per cent).

It will be observed that the number of bands recorded in the table is referred to as corrected. For before commencing the experiments it is essential, as Warburg and Koch pointed out, to determine whether there is any bending of the parts of the apparatus, recorded by the movement of the interference bands ; a preliminary experiment is made with the same loads as are to be used in the determinations, but with a thick relatively unbendable block of glass instead of a thin plate. With the author's apparatus this correction is reduced to very minute dimensions, only just attaining the equivalent of a single interference band for the maximum load of 500 grammes. The actual values of the correction are : for 500 grammes 1·04 band, for 400 gr. 0·86 band, for 300 gr. 0·69 band, for 200 gr. 0·51 band, and for 100 gr. 0·26 band. Special provision for lowering the balance by the depth of the block of glass one centimetre thick is made, in order that this correction can be determined, a metal packing plate also one centimetre thick being inserted during the construction between the balance pedestal and the rectangular box on which it stands ; this plate is temporarily removed during the determination

of the correction, lowering the pressure-point to just the right amount for it to come under the glass block when the latter is in contact with the platinum-iridium knife-edges.

We may now work out for the example of pyrites the actual value of E, the modulus of elasticity, that is, the coefficient of resistance to bending or dilatation, by use of the formula of Warburg (see page 1335),

$$E = \frac{PL^3}{4st^3b}\left\{1+3\left(\frac{t}{L}\right)^2\right\}.$$

The experimental data are :

$P = 100$ grammes,
$L = 17{\cdot}261$ millimetres,
$b = 8{\cdot}833$,
$t = 0{\cdot}875$,
$n = 2{\cdot}27$ bands,

$$s = n\frac{\lambda}{2} = 0{\cdot}0007448 \text{ millimetre.}$$

The result for E is found to be, for the direction normal to the cube face, that is, along any cubic axis :

$$E = 29\ 172\ 000 + 225\ 000 = 29\ 397\ 000.$$

An approximate determination by Voigt, by the older method, with a similarly orientated plate of pyrites from Cornwall gave the value 35 500 000. Other results of Voigt's, however, were much lower, and very similar to that derived from the author's experiments. Pyrites crystals would, indeed, appear to show considerable differences in elasticity, possibly due to cavities and enclosures. In any case the coefficient E of resistance to bending or dilatation is exceptionally high, which accounts for the very small number of interference bands which effect their transit for 100 grammes of load, compared with the considerable number usually observed with a plate of the same dimensions of other substances. Indeed Voigt states that his " Dehnungskoëfficient " E (the reciprocal $\frac{1}{E}$ of our E) for pyrites, which he gives as $2{\cdot}83 \times 10^{-8}$, is the smallest yet observed. The value of this reciprocal afforded by the author's determination is $3{\cdot}40 \times 10^{-8}$.

Determination of Torsion.—The Modulus of Torsion F, corresponding to Young's Modulus of Elasticity E, is given by the following formula, according to Kohlrausch :

$$F = \frac{2\pi}{g} \cdot \frac{Kl}{t^2r^4},$$

in which g is the acceleration of gravitation and $= 9810$, l is the length in millimetres of the wire of the substance (the usual form in which the substance is employed in torsion experiments), and r its radius also in mm., K is the moment of inertia of the twisting (rotating) weight in kilogrammes

round the axis of rotation, and t is the time in seconds of an oscillation, supposing the weight to be suspended from (hung on) the wire and set in rotating vibration round the vertical axis (the wire itself). This mode of dealing with torsion by use of a wire, so convenient for metals, is obviously impossible of application to crystals. A rod of rectangular or circular section, or a prism or slab of rectangular section, are the only forms suitable in the case of crystals.

As already stated on page 1337, the best apparatus hitherto devised for the determination of the torsion of crystals, suitable for use with a rectangular rod, prism, or slab, is that of W. Voigt. The formula employed by Voigt as expressing the torsion law is :

$$\theta = \frac{3TNL}{t^3 b\left(1 + \frac{t}{b}f\right)},$$

where θ is the torsion angle, T is the torsion coefficient for a prism or slab of the substance of rectangular section, N is the rotation moment of the couple employed to effect the torsion, and L, b, and t are the free length, breadth, and thickness of the prism or slab as in the formula for E the modulus of elasticity ; f is a function of the sectional dimensions b and t, which is constant when the ratio of $b : t$ exceeds 3, and can be eliminated by a combination of observations. The formula is correct as it stands when the slab or prism has its length normal to a symmetry plane or parallel to a symmetry axis of the crystal. It requires some correction factors to be added, however, when the length is oblique to a crystallographic symmetry plane or axis.

Voigt's Torsion Apparatus.—The apparatus of W. Voigt is shown in Fig. 901 (one-third size). It consists essentially of a pair of similar and parallel wheels a and a', arranged on a common axis at the two ends of the apparatus. They are intended for alternate use, so that either can be used to deliver the torsion to the bar of the crystal or other substance under investigation b, which lies between them along their axis. Each wheel is rotatable between points supported in trestle bearings c and c', the base of each pair of which is capable of sliding along the rigid base-bar d, so as to vary the distance of the wheels apart to suit crystal bars of different lengths. The one not in use for the moment as twisting wheel is to be clamped by the pairs of screws ee or $e'e'$. The rotation of the wheel in use is effected by means of a couple provided, in a readily recognisable manner, by the weights placed in the balance pan f; the latter is suspended from the beam g, one end of which is attached to the band working the wheel, and which passes first over an intervening third similar wheel h, supported on a column k. The base of this column is a slider over the front bar of the basal rectangular frame l, so as to enable it to be placed opposite that wheel (of the pair) which is to be used as twister. The operation of the weight is controlled by the apparatus below the frame, consisting of a wire m, worked by an ordinary door-bell puller, which actuates an eccentric n, which in turn raises or lowers slightly the rod o passing through a link in the short chain suspending f from g.

The crystal bar b to be twisted is clamped at each end in a small gripper qq' which is rigidly connected with the wheel by a claw rr', passing without contact over the upper narrow end of the inner upright of the trestle support. Adjustments are provided to enable the crystal bar b to be brought so that its axis is identical with

that of the two wheels *aa'*, that is, identical with the axis of rotation and of torsion. The measurement of the torsion suffered by the bar, on the application of the couple to one of the wheels, is carried out by means of a telescope (not shown in the figure), and a scale reflected into the latter from the mirrors *ss'*, which are attached directly to the crystal bar *b*, and not to the grippers *qq'*; for even with the most careful clamping by the latter there is always some slight "give" or motion in the fastenings. Each mirror carries a sharp pair of tongs, or fork, clamped on the bar, which is here faced with tinfoil in which the edge of the forked fitting presses a fine line, serving to indicate the exact end of the bar-length the torsion of which is being determined. For the distance between the two marks in the two little tinfoil attachments is taken as the relevant length of the bar, and used as such in the calculations. By means of the

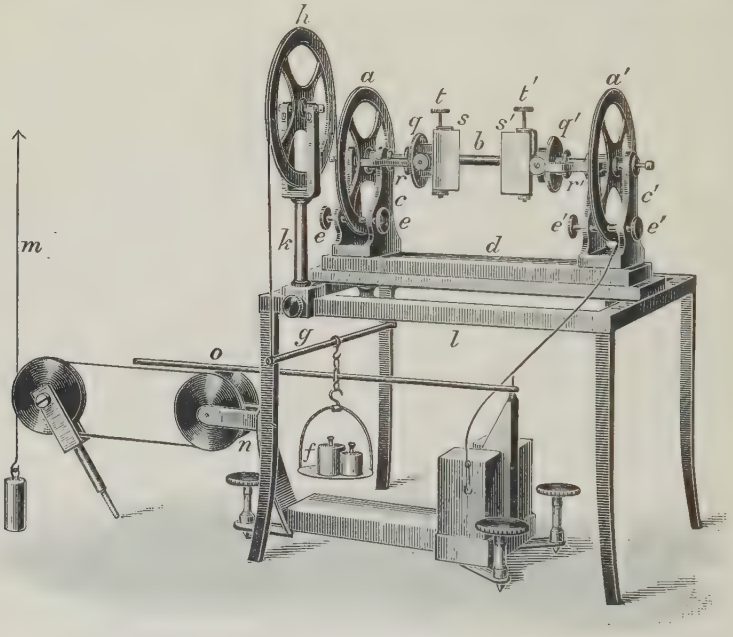


FIG. 901.—Voigt's Torsion Apparatus.

milled heads *tt'* the two mirrors can be regulated so that the two images of the scale reflected from them, the relative movement of which affords a measure of the torsion suffered by the bar, are brought simultaneously into the field of view of the telescope. A movement of the scale of one millimetre corresponds to a torsion of 20 seconds of arc.

Principle of the Interference Torsometer.—The torsion apparatus now under construction for the author is a refinement of the Voigt apparatus in the following particulars, which it is hoped will render it sufficiently delicate for use with relatively very small crystal bars, say two or three centimetres of relevant length, as in the case of the plates for the elasmometer.

(1) It is constructed on a somewhat smaller scale, but with great mechanical accuracy and delicacy, so as securely to grip and apply torsion

to such small crystals as have just been referred to, instead of being applicable only to such naturally occurring mineral crystals as are obtainable in considerable size. These latter, however, may also be readily used, and when available are naturally preferable.

(2) Instead of the mirror method of magnifying the torsion by reflecting a scale into a telescope, the torse movement at the two relevant endpoints is communicated to two horizontal sliders, each carrying a very finely engraved fiducial mark, the movement of which is observed, followed up, and measured in interference bands, with the aid of a travelling microscope carrying one of the interference surfaces, as in the Interferential Comparator to be described in the next section.

(3) The method of applying the weight used to produce the mechanical torse-couple is to be similar to that employed in the case of the elasmometer.

The Interferential Comparator referred to in (2) above is an apparatus designed by the author for the Standards Department of the Board of Trade, in compliance with a request to adapt the interference interferometer used in the dilatometer and elasmometer to the comparison of standards of length. The success which attended the effort, and the experience therein gained, showed that the optical portion of the comparator (omitting the second microscope) provided a perfectly general method, of the utmost refinement yet attained, for the measurement of small amounts of motion of any kind whatsoever. As these optical parts of the comparator are immediately suitable for use with a torsometer, without any modification other than their mode of basal support, it will be best to describe first the essential features of the comparator.

The Interferential Comparator for Standards of Length.—There is no necessity for Part B of the interferometer (Fig. 894, page 1331) to be vertically suspended, when used for purposes other than those of the dilatometer and elasmometer, and an excellent example of its horizontal employment, the whole optical arrangement being then horizontal, is afforded by the Wave-Length Comparator for Standards of Length which was installed under the author's direction in the year 1909 at the Standards Department of the Board of Trade. For full details of this instrument the author's memoir[1] should be consulted, but as the apparatus has many points which will prove very useful in future crystallographic investigation, and the optical portion is already being duplicated for the author's own laboratory, for use with the torsion apparatus, a brief description will next be given.

Fig. 902 gives a general view of the whole comparator, and Fig. 903 shows the essential parts as far as the right-hand half of the apparatus is concerned, the omitted left half including the second microscope. Fig. 903*a* gives the arrangement of the glass interference plates and their supports and adjustments, about a horizontal optical axis. Part A of the interferometer (Fig. 894), standing to the extreme right in Fig. 903, is exactly as already described.

The large wheel with divided circle to the right of the centre and on the immediate left of Part A is the driving wheel for the very fine movement of a travelling microscope, the minute amount of motion of which is to be measured in interference bands, and to

[1] *Phil. Trans.*, A, 1909, *210*, 1.

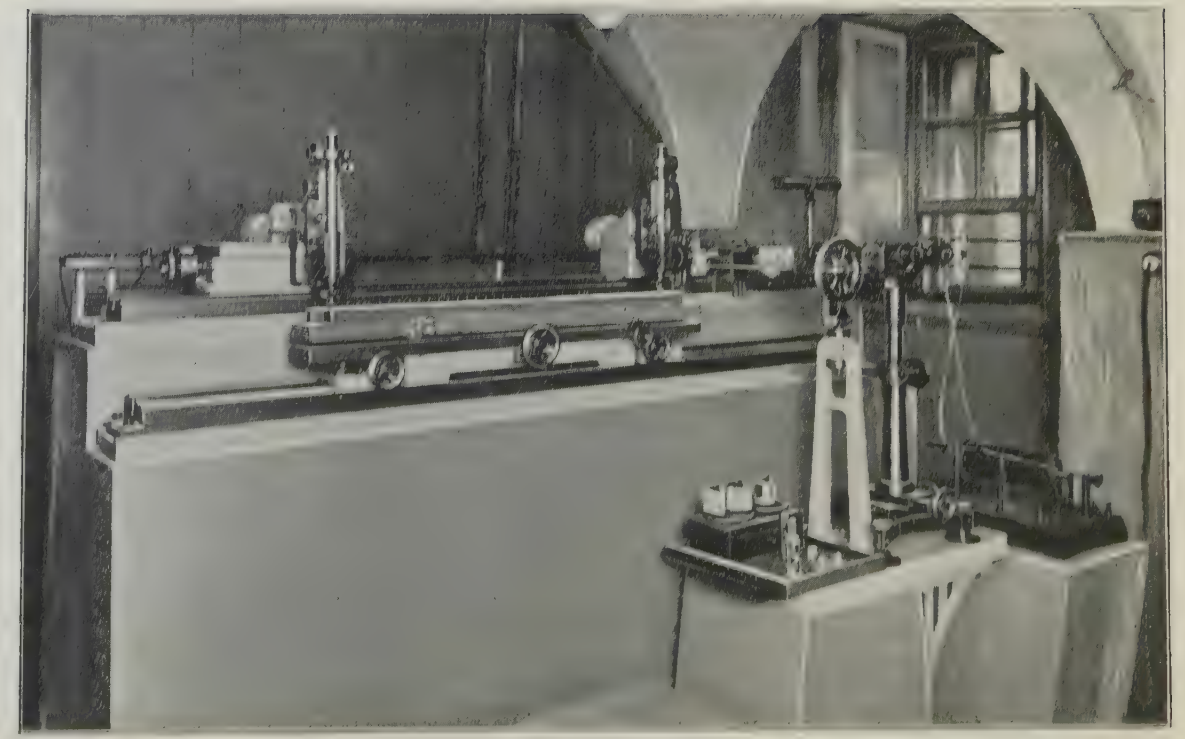


FIG. 902. - The Wave-length Comparator for Standards of Length.

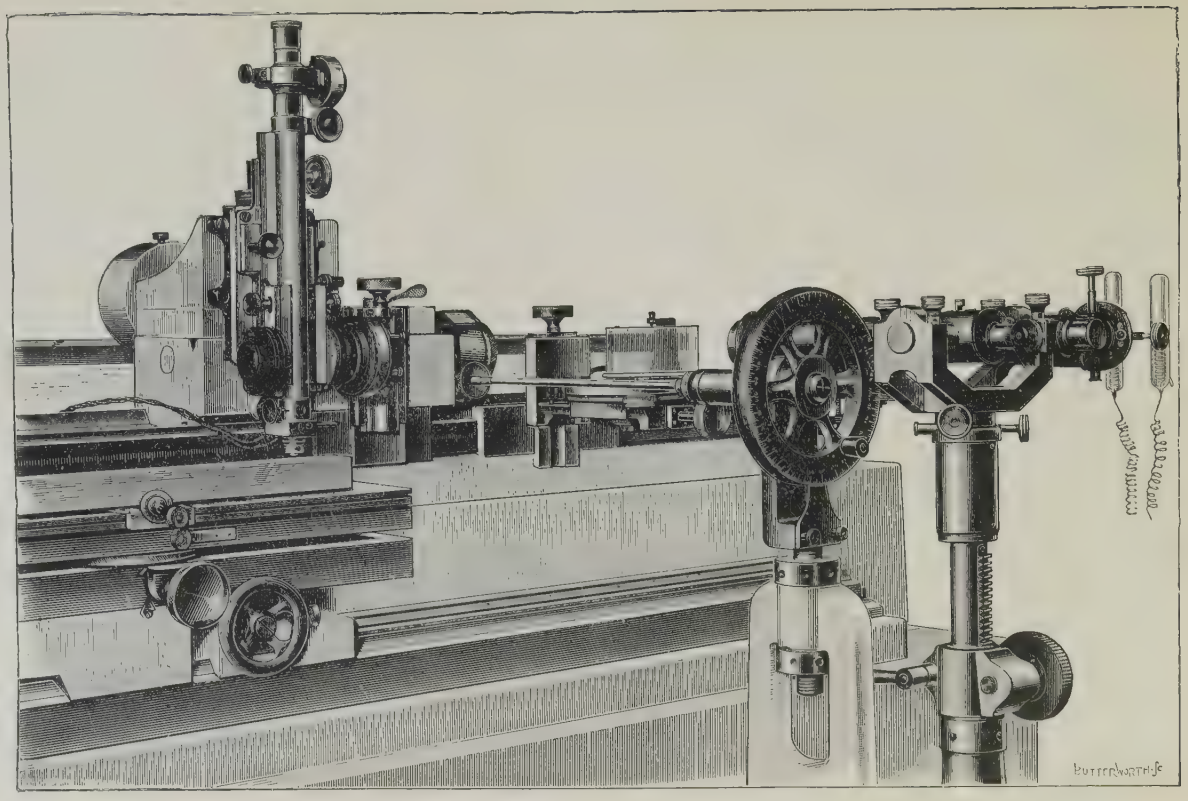


FIG. 903.—Right-hand Part of Comparator, showing Interferometer.

which the movable black glass disc (the polished surface of which reflects one of the interfering rays) of the interference apparatus is rigidly attached. This microscope is the right-hand one of a pair of similar microscopes, arranged above the two ends of the standard bar under observation. For instance, the Imperial Standard Yard, constructed of Baily's metal (16 parts copper, 2½ tin, and 1 of zinc), and one inch square in section, is shown in position in Fig. 903. One microscope is arranged over each of two little gold studs, countersunk in holes half an inch deep (that is, to the position of minimum flexure) and on which the defining marks indicating the limits of the yard are engraved, about one inch from each end of the bar. The two microscopes, of which only the right-hand one is shown in Fig. 903, are carried on heavy blocks which slide on a very rigid V-and-plane bed; both the microscopes on the blocks, and the latter on the bed over which they slide, are arranged complementarily, in a right- and left-handed, laterally inverted, manner, the microscopes being near the inner ends of the blocks (so that they can be brought very close to each other when measuring small objects), and the driving screw heads at the outer ends for convenience of manipulation. Each microscope carries two of the

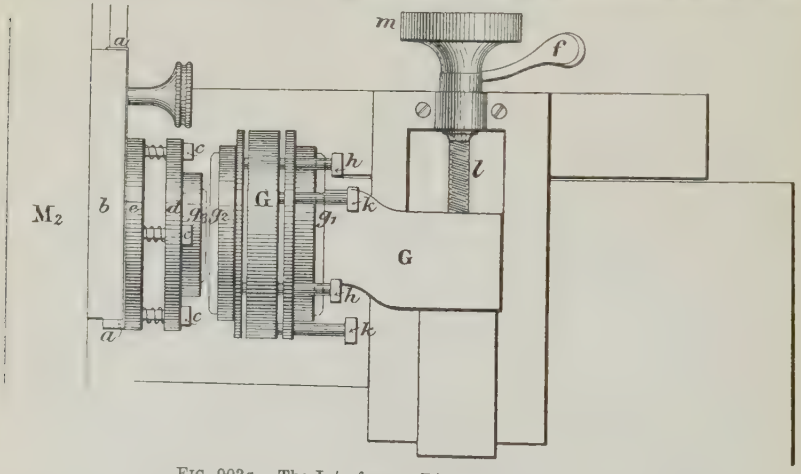


FIG. 903*a*.—The Interference Discs of the Comparator.

black glass discs, one on each side, just above the height of the objective, the one on the right of the right-hand microscope being usually the only one in operation, marked g_3 in Fig. 903*a*. The other interference discs g_2 and g_1, of colourless glass, are carried independently, as shown in Fig. 903*a*, by a fitting attached (with possibility of tight sliding and then fixation) to a dove-tail rib running along the side of the bed.

The dispersing apparatus in this instrument is a very large Hilger constant deviation prism (see page 966 and Fig. 718), instead of the train of two refracting prisms; it is carried on an adjustable and divided goniometer table, and is horizontally arranged along the same axis as the interference discs, being supported in an adjustable manner, with possibility of sliding and fixation, along the same dove-tail rib carried along the front face of the V-and-plane bed. The interference apparatus, shown best in Fig. 903*a*, consists essentially of three truly plane thick glass plates g_1, g_2, and g_3. The two marked g_1 and g_2 are of colourless glass, 5 cm. in diameter and 1 cm. thick, with the two surfaces of each inclined 35 minutes to each other; they replace and act as the cover-wedge and dispersion-countervailing wedge-disc of the interferometer as already described. They are mounted about a fixed thick metallic disc-annulus G, in a manner which permits the adjustment of each glass plate about

the disc by three screws, h for one plate and k for the other; the disc has a central circular clear aperture of one inch diameter, corresponding to the diameter of the polished surface of the black glass plate g_3. The carrier (also marked G) of the disc is also vertically adjustable by the screw ml, and fixed by the clamp f. The dispersion-countervailing disc g_1 is adjusted sufficiently out of parallelism with the interference disc g_2 to get rid of the reflections from its surfaces, and the 35′ inclination of the back surface (furthest from the microscope) of g_2 to the front surface is adequate to eliminate also the reflection from this back surface. The front surface (nearest the microscope) of g_2 is the important one which is relevant to the interference, and it carries at its centre the little silvered ring the centre of which is the reference centre; it is adjusted to approximate parallelism with and to about three-quarters of a millimetre distance from the outer polished surface (also relevant to the interference) of the black glass disc g_3 carried by the microscope (the inner surface of this latter disc not being required and therefore ground dull). The black glass disc g_3 has been once for all arranged so that its polished surface is truly perpendicular to the horizontal optical axis of the system, and parallel to that of the microscope. The surface g_2 is adjusted with the aid of the three screws h, for the production (by the mutual interference of the reflections from g_2 and g_3) of a field of interference bands of suitable width, and upright in the field of view (as in Fig. 891), parallel to the vertical pair of spider-lines, when viewed through the micrometer eyepiece of the interferometer telescope. Red hydrogen or yellow neon light is conveniently used during these adjustments and for purposes of demonstration, but red cadmium light is employed in actual measurements, that limb of the H-shaped Geissler tube which contains the small piece of cadmium being heated to a temperature of 200° to 250° C. in order to volatilise the metal.

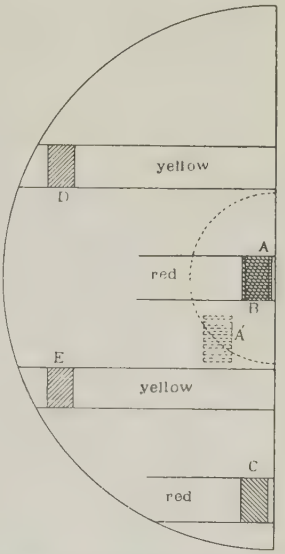


FIG. 904.—Positions of Signal-images from the Five Surfaces.

The correct adjustment is illustrated in Fig. 904, which represents the positions of the five images of the signal-stop of the interferometer telescope reflected from the five glass surfaces, as seen when the simple eyepiece is used instead of the band-viewing ocular. A is the image from the black glass surface g_3, and is best allowed to remain fixed, as this surface has been once for all carefully adjusted by its own little adjusting screws so that it is exactly normal to the horizontal optical axis of the optical train; B and C are from g_2, and D and E from g_1. A and B are to be brought to overlap as shown in the figure, by use of the screws h adjusting g_2, the overlap being nearly but not quite laterally complete, while vertically exactly complete. A′ shows the sort of position A usually occupies when first found, assuming approximate adjustment to have been effected; it is rarely further away than this, and can readily be brought to its proper position A by use of the adjusting screws h. When g_1 is also adjusted by the screws k so that the images are arranged as shown there can be no interference by the four spectra from g_1 and g_2 with one another. The adjustment, as a whole, of the thus arranged set of five images—so that A and B occupy the central position, as in Fig. 904, and are alone within the small dotted circle representing the iris aperture, while the other images C, D, and E are all excluded by the iris diaphragm—is effected by the adjustment of the whole telescope for height, azimuth, and altitude.

The V-and-plane bed on which the microscopes travel, and to a dove-tailed rib

(engraved with a scale) extending along the whole front of which the interference apparatus and constant deviation prism fittings are attached, is of specially chosen cast iron, 6 feet 6 inches long, and most carefully worked as regards the V-and-plane surfaces. It rests in a plinth of the same metal, bolted down to the upper surface of a stone block 7 feet 6 inches long, 4 feet 4 inches high above the floor of the room, and 2 feet 2 inches thick at the base. This in turn rests on a concrete basal block going right down 4 feet to the foundations, with an isolating air space of 6 inches all around.

Each microscope is mounted on a thick horizontal-fine-movement sliding slab, also of the same cast iron, 10 inches long, the movement of which is brought about, with no trace of backlash owing to a special device, by the all-important finely pitched screw, with V-and-plane contact, over a similar but thicker block of steel (for smooth sliding) 11 inches long; this in turn slides on the V-and-plane bed, thereby affording the coarse adjustment. The fine screw of half-millimetre pitch (1/50th inch) carries near its end a large silver drum-head, graduated directly into a thousand parts by a method which will be found fully described on page 1344; at the actual end of the screw a large milled head is provided for quick hand-rotation of the screw and consequent relatively more rapid traversing of the microscope when the excessively slow rotation is not required, as when effecting preliminary rough adjustments. The screw also carries, just before the drum, a driving worm-wheel with 100 teeth, gearing with an endless screw for effecting the slow driving, the shaft of which is prolonged in front, and connected by means either of a rigid steel shaft or more conveniently by a flexible coiled steel-wire tubular shaft to the axle of the large divided wheel seen in the right foreground in Fig. 903, by rotation of which the traversing of the microscope is actually effected. Each complete revolution of the wheel corresponds to the traverse of the microscope and its black glass disc for 0·005 millimetre parallel to the bed and to the length of the standard bar under observation, a movement which is accompanied by the passage of 15 interference bands of red hydrogen or cadmium light. Thus more than an inch of movement of the circumference of the wheel is required to effect the passage of each band, a degree of delicacy of control which is very convenient and satisfactory. The passage of the bands occurs with perfect steadiness, parallel to themselves upright in the field of view and parallel to the pair of vertical spider-lines of the micrometer eyepiece. The field of interference bands (shown in Fig. 891 on page 1311) afforded by this instrument is magnificent, and the hundredth part of the width of a band (distance between centres of two adjacent bands), corresponding to a movement of the microscope of approximately one eight-millionth of an inch, can be read off from the eyepiece micrometer with the greatest facility. The flexible shaft is a great satisfaction, as it avoids all strain and yet delivers the motion of the wheel with surprising perfection and absence of lag.

Another large cast-iron V-and-plane bed rests in a plinth, like the upper bed, bolted down to the stone block, in a step cut out of the latter below the top in front. This carries an elongated narrow adjustable table for the support of two bar measures, for instance, the standard bar and a copy which it is desired to compare with the standard bar, as shown in Fig. 902; the table is provided with both quick and fine adjustments for its longitudinal movement and variation of its horizontal position on the bed, and also with a traversing motion perpendicular to its length (a very smooth movement in V-slides, one near each end at the Airy positions for rigidity), a fine adjustment for azimuth, and another for level. There are three interchangeable table tops; one is a truly plane experimental slab, another is fitted with friction rollers, in the approved manner and at the right positions (symmetrical points near each end determined by the Airy formula[1]) for minimum flexure, for the independent and simultaneous

[1] The well-known formula of Sir George Airy is $d = l/\sqrt{n^2 - 1}$, where d = the distance between the supports, l = the length of the object supported, and n = the number of supports.

support of two line-measure bars, and a third provides for the support of a line-measure and an end-measure.

The whole room in which this interferometric comparator for standards of length is installed is controlled by an electrical thermostat, so that the temperature remains always at 62° Fahrenheit (16·66° Centigrade), the temperature at which all comparisons and measurements are required to be made. For the whole period of the several years which have now elapsed since the installation was completed (in the year 1909), the thermograph has recorded an absolutely straight line, that for 62° Fahrenheit.

In order to compare two bars, (1) the standard bar is arranged on the adjusting table so that the two defining lines near the ends of the bar are focussed by the two microscopes and adjusted to the spider-lines; (2) the standard bar is replaced by the bar to be compared (already in position parallel to the standard bar), by use of the front-to-back traversing movement of the table, and the left-hand defining mark is adjusted under its microscope by the longitudinal movement of the table; then, if the right-hand defining mark is not also thereby found to be automatically in proper adjustment under the right-hand microscope carrying the black glass interference disc in use, as it will only be when the copy is absolutely an exact replica of the standard, (3) that right-hand microscope is traversed until it *is* so adjusted, by rotation of the large fine-adjustment wheel (in front and slightly to the right in Fig. 903) which effects the excessively slow and steady movement of the slider carrying the microscope; (4) this third process is accompanied by a corresponding and simultaneous passage of interference bands, and these are viewed through the telescope and counted as they pass the reference spot, the centre of the miniature silvered ring at the centre of the relevant reflecting surface of the large colourless glass disc g_2 of the interference apparatus, and measurement of any final fraction of a band is made with the aid of the micrometer and its pair of vertical parallel spider-lines, a similar determination of any initial fraction having been made before carrying out operation (3).

The fineness of the sliding movement of the microscope, its absolute steadiness, and the perfect control over it, are the essential features of this application of the author's form of interferometer, which have rendered it so successful as regards its specific object, and have constituted it the most accurate measuring instrument in existence at the present time. It was constructed by Messrs. Troughton & Simms.

A further reference to the instrument will be found on page 1373, regarding the use of the high powers specially supplied with the two microscopes for use with the Grayson rulings of 40,000 lines to the inch on speculum metal, and the value of these rulings as defining lines of extreme refinement for standards of length, comparable with the delicacy of the method of measurement in wave-lengths of light. For the one forty-thousandth of an inch is the wave-length of red light, and corresponds to the passage of two interference bands only (in red cadmium or hydrogen light), whereas the defining marks on the Imperial Standard Yard, although exceedingly fine scratches quite satisfactory for the finest mechanical modes of measurement, are of such a thickness as corresponds to the passage of no less than 45 interference bands, and even the finest marks on the more recently constructed (1902) copy, a bar of Tresca-shaped section (between H and X shape) constructed of platinum-iridium, correspond to the passage of 15 interference bands. It will be shown in the next section that these rulings, 40,000 to the inch, are capable of being utilised in the torsometer,

or any other fine measurement requiring a fiducial mark. Fig. 905 shows the appearance of such a fiducial defining-line signal, or "location signal," composed of five rulings 1/40,000 of an inch apart, ruled for the Standards Department by the late Prof. Grayson (whose early demise is most regrettable). The central line (the third) of the five seen close together in the central part of the figure is the actual defining line, and when all five are clearly resolved this central line, as indeed are all five, is quite sharply separated from its companions on either side, using the 1/15th inch dry objective supplied by Mr. Conrad Beck. The two stronger vertical lines and two similar horizontal ones are coarser rulings added to aid in first locating the signal under a lower power, a $\frac{2}{3}$-inch objective being especially suitable. The single horizontal diametrical line, and the pair of vertical ones to the left of the five fine rulings, are the spider-lines of the micrometer, and the vertical pair can be readily brought to isolate and centre the third (middle) all-important line of the five rulings, the actual defining line.

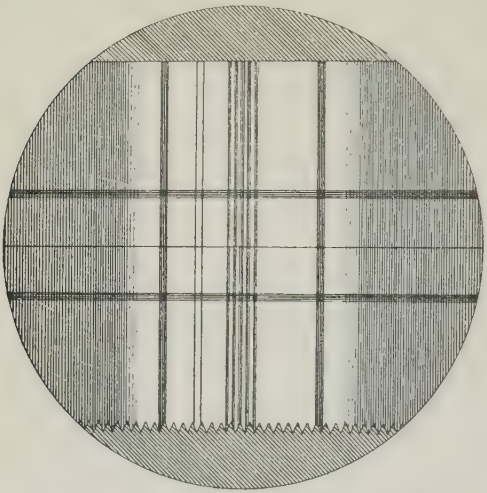


FIG. 905.—The Grayson-ruling Location Signal or Fiducial Mark.

The necessary illumination of the rulings, or whatever fiducial mark is under observation, or opaque objects in general, is afforded by a clear, thin, truly plane and parallel-surfaced glass reflector, carried in the microscope tube just above the objective and adjustable from without by a graduated milled head; a little adjustable tube carrying an iris diaphragm at the end nearest the reflector, and a lens at the other outer end, enables the light from a Nernst lamp at some distance, filtered through copper sulphate solution, to be concentrated by the reflector on the object to be focussed. The intense greenish-blue light afforded proves admirable for effecting the maximum possible resolution of Grayson rulings, and very pleasant to the eyes, avoiding all strain.

The Torsometer.—The following parts of the comparator as just described are being reproduced for the purposes, among many others connected with crystal research, of the torsometer now under construction. They comprise 2 feet 6 inches of the right half of the upper V-and-plane bed and all that it carries, namely: (*a*) An exact duplicate of one (the left one) of the two travelling microscopes, with fine screw movement complete, and carrying the black glass disc g_3 (Fig. 903*a*) which furnishes one of the two surfaces relevant to the interference. (*b*) The colourless

glass interference discs g_1 and g_2 and their supports and adjustments. (*c*) The constant deviation prism and its rotating table and adjustments. (*d*) A sufficient length, 2 feet 6 inches, of the V-and-plane bed on which the microscope block travels, and to a dove-tail along the front of which (*b*) and (*c*) are attached. (*e*) The large wheel for actuating the movement of the driving screw of the microscope by means of the connecting flexible-coil steel shaft. In addition, of course, there is (*f*) the interference telescope, with its Geissler tube and adjustable stand, already provided for the purposes of the dilatometer and elasmometer, as shown in Figs. 888 and 890 and at A in Fig. 894.

The V-and-plane bed (part *d*) with the parts *a*, *b*, and *c* that it carries, is mounted on a truly plane iron plinth as in the comparator, but of only the same length, 2 feet 6 inches, as *d*. This plinth is carried by two stout supporting pillars of considerable extent backwards, and arranged at the Airy positions, above a cast-iron rectangular base-plate 28 by 34 inches in size and of great rigidity, so that the large hollow central part or arch will afford ample space for the accommodation under the microscope of the specific apparatus which carries the object, the movement of which is to be measured, in this case the torsometer proper carrying the crystal bar and the means of applying torsion to it. The wall-like pillars forming the sides of the arch spread out into capitals above and plinths below, and as they descend towards the base they deepen considerably backwards, leaving ample working space in front, while affording a very solid and rigid support for the whole structure, being finally bolted down to the base-plate of the whole apparatus.

The torsometer proper is not to rest directly on this ground plate, but on an adjusting table, which is to serve for the adjustment under the microscope of whatever object—on its special carrying apparatus—is to be brought to measurement. This adjusting table is as large as can be conveniently accommodated under the arch ; it affords three horizontal movements, two of them being rectangular and worked by two screws with wheel heads affording 2 inches of fine adjustment, sideways and back-to-front, the latter supplemented by extensive coarse adjustment in dove-tailed guides ; and the third being a circular movement worked by a large milled-headed screw, all these screws being fitted to act with the minimum of backlash. It is also adjustable vertically for height, by levelling screws affording two inches of possible vertical adjustment.

The interferometer telescope with its Geissler tube attachment is to be mounted separately, in front, on the right, and directed to the constant deviation prism, set for the passage of light of the particular wave-length (of hydrogen, neon, or cadmium) to be employed in producing the interference bands. On the left, leaving ample working space in the middle of the front, is to be placed the large fine-movement control wheel, by which the endless screw of the driving worm-wheel for the fine movement of the microscope is worked, a flexible-coiled steel shaft forming the connection as in the case of the comparator. The wheel is to be mounted on its own very rigid stand. The fact that the microscope is a duplicate of the left-hand one of the comparator rather than the right-hand one affords much more working space in the middle front of the apparatus, between the wheel on the extreme left and the interferometer telescope on the extreme right.

The torsometer proper is intended to be similar to the apparatus of Voigt as far as that portion of it on the top of the rectangular frame-stand is concerned, shown in Fig. 901, page 1350. The legs of the stand are to be omitted, however, being replaced by four levelling screws, one at each corner of the frame, which will rest directly on the adjusting table above described, and are to be secured thereon, after use of the levelling screws, by locking screw-clamps. The frame and all that it carries,

however, are to be somewhat smaller than in Voigt's apparatus, and the parts very delicately constructed, although rigidly, so as to take not only fairly large bars similar to those used by Voigt (when available) but also quite small crystal bars.

The weight-applying apparatus is to consist, as in the elasmometer, of a balance pan, directly suspended from the cord passing over the front wheel in Fig. 901, carrying from the upper bar of its suspension frame a soft string loop, from which the weight of which the torsion effect is to be measured is to be gradually hung by its hook (which replaces the usual knob in the set of platinised weights supplied with the elasmometer), with the aid of the vertical fine movement of the little table on which the weight rests in the first instance, as shown to the right in Fig. 898 on page 1340. The damping disc dipping in a dish of cedar oil, carried below the pan when used for the elasmometer may not be required when used for the torsometer, but is available if desired for experimentation purposes. The pan is to be retained, however, for the reception of the initial constant weight or weights with which it may be desired to commence the determination.

In the place of the two mirrors and their forked carriers of the Voigt apparatus there are to be two very delicately constructed gripping tongs, each tightly clamped to the bar and provided, as in Voigt's apparatus, with straight edges which press a mark in a fragment of tinfoil attached to the bar. Each is to be fitted with a radial arm, which can be adjusted to, and fixed very rigidly at, any desired position, and will usually be arranged at the commencement of a determination truly vertically (when the initial constant weight is in operation), so as to project upwards above the bar. When torsion is applied to the crystal bar, this little vertical arm will naturally move with the twisted bar slightly to one side, and in doing so it is to be made to communicate its motion to a very light horizontal slider carrying the fiducial mark to be observed through the microscope. The arm edge is always to be maintained in close contact with the straight-edge end of the slider, by means of a light spring, fitted in a cavity in the guiding bed and pressing against a projection carried by and under the slider. The other end of the slider is to carry a small square black glass disc (about 8 mm. square) attached in a manner adjustable by three screws, so that its reflecting surface may be adjusted exactly vertical and perpendicular to the length of the slider. This will enable an alternative mode of measurement to be adopted when the amount of torsion is exceedingly small, namely, by using these two little black surfaces, adjusted absolutely parallel to each other, directly with the colourless glass surface of g_2 for the production of interference bands, instead of using the microscope and its black glass disc at all. The microscope can easily be removed out of the way, by hand sliding along its V-and-plane bed, and also both the colourless interference discs fitting and the constant deviation prism fitting can be lowered if this be needful in order to bring the disc g_2 and the slides on the same level, so that the little black discs (close together and with their surfaces in the same plane) can be brought up to within the necessary millimetre or so of distance from the surface of g_2.

Several pairs of these sliders are to be provided, carrying fiducial engraved marks of various degrees of fineness. The most refined, intended to be used in the actual determinations of the torsion of crystal bars, is of the character described on page 1357, consisting of five Grayson rulings 1/40,000th of an inch apart, as shown in Fig. 905, the middle one (the third) of which, as already mentioned, is to be regarded as the actual fiducial mark or signal. These rulings were made on speculum metal by the late Prof. Grayson in Melbourne, and the small rectangular plates of speculum on which they are ruled are mounted with a suitable cement on the top face of the slider. The rulings are very clearly defined by the microscope when the Beck 1/15th-inch dry objective is employed, as in the case of the comparator.

The supporting guides for the two parallel sliders are to form part of a columnar readily removable attachment to whichever bar of the frame is on the right when the apparatus is in position under the microscope. The sliders themselves are

elongated rectangular in shape, with flat tops and V-and-plane shaped below, corresponding to the V-and-plane beds over which they glide almost without friction. The end to be in contact with the pushing arm-edge is in each case a true straight-edge accurately perpendicular to the length of the slider, and the other end carries the black glass interference disc as just described. Sliders in steel, agate, and aluminium (or a harder alloy containing aluminium) are to be provided, and experience will teach which are most useful and convenient and afford least friction. The parallel pair of V-and-plane guide supports for the sliders are adjustable for their distance apart, to accommodate crystal bars of different lengths while preserving strict parallelism, by suitable screw motions.

The untimely death of Professor Grayson, and the probability of difficulty being experienced in obtaining more of the wonderful rulings by his machine, together with the fact that it has been found possible in the case of the comparator to adjust each band, one after the other, exactly to the reference centre and to maintain it there for quite a long time, by the fine movement of the microscope carrying the black glass surface (of the two surfaces concerned in the interference), have decided the author to add a ruling apparatus to the instrument now under construction. It is to be carried by the same V-and-plane slab as carries the microscope, but readily detachable when not required. It will then be possible, as each band is adjusted, to rule a line, using the finest obtainable diamond point, selected as described on page 1170. Such a series of rulings would be the 1/80,000th of an inch apart, and would be too fine for practical use. But lines ruled corresponding to every second band, which would be easier to produce, corresponding to the 1/40,000th of an inch apart, are just what are needed, and it is for the purpose of making such rulings that the ruling apparatus is being added. Rulings prepared in this manner, actually ruled directly against interference bands, ought to possess quite a special value as regards accuracy of spacing and knowledge of their exact distances apart.

The torsometer proper will be a symmetrical instrument (or capable of being made so by proper adjustment of the movable parts) about a vertical plane of symmetry parallel to the ends and passing through the centre of the crystal bar. Hence it will be reversible by rotation for 180° in the horizontal plane and about the vertical axis, so that torsion may be applied at either end, that end being brought near to the observer and the other end inserted under the arch.

The method intended for the use of the instrument is that a series of couples of increasing force shall be applied to the crystal bar, by the wheel at the end nearer the observer, the bar being held at its two ends in the grippers with its axis parallel to, and identical with, that of the two (near and far) wheels. The weight in each case is to be gradually let down into action in its string loop (attached to the frame of the pan suspended from the third movable wheel) by the fine-movement of the tabular ended arm on which the weight is first placed. The angular torsion produced at the two positions near each end of the bar, where the gripping edges of the little fitting mark the tinfoil attached to the bar, is to be communicated to the two respective sliders by the rigid vertical radial arm carried

by the fitting, as a tangential movement in each case. The far one of these two movements will be excessively small, and its terminal point is to be regarded as the zero; while the movement at the near position will be relatively larger, but still small. These movements are each to be measured in interference bands by following up the fiducial mark in each case with the travelling microscope, counting bands the while, the end of the movement being determined when the cross spider-lines of the microscope are once more adjusted over the central line of the five Grayson signal rulings. One of the sliders, preferably the far one, will have already been in position under the microscope, and the second, the near one, is to be pushed in and adjusted underneath the microscope by means of the back-and-front movement of the adjusting table, which is effected truly parallel to the axis of the torsometer. It is only necessary to traverse further the microscope from the terminal position of the first (far) slider to that for the second (near) slider, until the signal of this latter slider is in turn adjusted to the spider-lines, in order at once to obtain the differential tangential movement between the two positions on the bar marked by the gripping edges. For the actual tangential distance d is obtained by multiplying the number of interference bands by the semi wave-length of the light employed. This tangential distance d is then to be converted into the actual torsion angle θ by means of the formula $\tan\theta=\frac{d}{r}$, where r is the radius of the circle, counted from the centre of the bar and axis of torsion to the point where, at the vertical initial position of the radial arm, its edge touches the knife-edge end of the slider, a length in millimetres determined once for all (the height of the axis of torsion and that of the contact straight edge of the slide being constant). As r is constant a table of angles corresponding to definite tangential lengths d can once for all be prepared, when the angle of torsion can immediately be read off.

A duplicate series of determinations with the same weights can then subsequently be made with the torsometer rotated 180°, and the couple delivered from the other wheel; that is, with the instrument laterally inverted under the arch so that what was formerly the near end is now the further one, and *vice versâ*, and with the auxiliary (third) movable wheel moved along the frame till it is opposite the other wheel, now also at the end which is nearest the observer, as is most convenient and where alone there is open space enough for it. A series of half-a-dozen different sets of such duplicate determinations will, of course, be made, in each of the two positions 180° apart in the horizontal plane, in order to be sure that concordant results are obtained and no sources of disturbance, such as cracks in the crystal bar, are operating. The true torsion can then be taken as the mean of the angles obtained as the results for the two cases, of the torsion being applied at the two different ends of the bar.

In the event of crystal bars of greater length than those usually alone obtainable being available, affording a torsion of corresponding larger amount than is conveniently counted out in interference bands, as, for instance, when the number of bands exceeds a thousand, the mechanical

movement of the microscope, which is recorded by the large silver drum in 1/2000th millimetre units, may be utilised. Also it will be quite possible as a method of intermediate refinement, to use a Grayson scale of 40,000 to the inch rulings for the purpose, each interval of which corresponds to two interference bands, and every tenth or fifth being ruled distinctly longer to assist in their counting. The interferometer need then only be used to determine the final fraction of a ruling in interference-band hundredths. Indeed the instrument affords, in the provision made in the optical part of the comparator which is utilised, and in the additional fittings and accessories provided, every possibility and variety of method of measurement, from the most accurate mechanical mode to that of the ultra-refined interference method, and that particular mode of carrying out the determination can be adopted which affords the necessary degree of refinement, having regard to the amount of experimental error which is observed, as indicated by the differences in the results of different determinations on different days with the same crystal bar.

When very small crystals are being dealt with, for which the amount of torsion even at the position of greater movement only amounts to a few readily counted interference bands, it will be possible to use the direct method without the aid of the travelling microscope, by utilising the two little black glass plane-polished disc-surfaces of which one is carried at the outer end of each of the two sliders. To get clear of the microscope it can be slid out of the way, and provision is made for lowering the two fittings carrying the colourless glass interference plates g_1 and g_2, and the constant deviation prism, respectively, from their positions opposite the black glass interference disc of the microscope to the lower level of the sliders. The interferometer telescope will also require to be lowered to the same level by its vertical rack-and-pinion movement. In all probability it will be possible to see the bands afforded by both the little black glass plates of the two sliders, close together in the field of view simultaneously, the diameter of field being such as will probably just take them in when side by side without much interval. The movement of both of the two sets of interference bands, corresponding to the torsion at the two positions where measurement is occurring, can then be followed at the same time.

It will also be possible to arrange for the movement of the crystal bar at the terminal relevant positions of the gripping edges to be communicated to two vertical sliders, by making the radial pushing arms take a horizontal position instead of vertical before the torsion is applied. The vertical sliders would be two close together, of similar type to the one shown in Fig. 899 on page 1342 in connection with the elasmometer. Provided the bar of crystal were not too large, and that the movement communicated to the vertical sliders were therefore relatively small, the control effected by the special control apparatus would be so good that no microscope would be required, and the measurement could be effected directly by the same vertical suspended tube (part B of Fig. 894) of the interferometer as is used with the elasmometer and the dilatometer.

It is intended to test this method in cases where very small crystals only

are available. The method in which the travelling microscope is used will, however, be the one of general application, for crystals of all sizes.

This chapter will close with a brief account of the interference phenomena utilised in the two other forms of apparatus, those of Michelson and of Fabry and Perot, as no account of interferometry could be considered complete without them; and also finally with the description of an interesting interference phenomenon exhibited naturally by crystals of mica, which by reason of its parallel plate or film structure exhibits directly effects similar to those afforded by the Michelson and Fabry and Perot interferometers.

Before passing to the consideration of these other interferometric methods, with which it is essential that the crystallographer shall be familiar, as they are bound to be used in future crystallographic research, in addition to the author's method, it should be stated that—

Three principles underlie all interferometry, and it will be convenient if these principles or different modes of working are first briefly laid down.

(1) When the two reflecting surfaces contributing to the interference are rigorously parallel, the light monochromatic and the thickness of the air-film (or other separating medium) not too great for the specific radiation used, and the telescope is adjusted for parallel rays (to infinity) and is directed normally towards the surfaces with its axis passing through their centres, a system of concentric circular interference fringes are seen, on looking through the telescope, around the centre of the field. The diameters of the rings obey the law of Newton's rings, with the difference that the order of interference diminishes as we pass outwards from the centre. The only essential condition about the incident light is that it must cover the field; it need not be composed of parallel rays. This method is suitable for great as well as small path-differences, up to the limits imposed by the degree of monochromatism (unresolvability) of the radiation employed. The rings are curves of equal incidence, as in the convergent light figures of uniaxial crystals. A simple plate of glass with parallel and silvered faces will serve, and almost equally well when only one face is silvered. The thickness of the medium-film is then of course fixed. Two plates are more convenient, however, to afford a possibility of varying the thickness of the medium (air)-film, and the two interior surfaces facing each other at close quarters, concerned in the interference, are usually silvered, while the two outer ones are not and are inclined at a very minute angle (a very few minutes) from true parallelism with the silvered surface of the plate in each case, in order to eliminate the light reflected from them out of the way. When the thickness of the air-film is increased by the retrogression of one of the plates parallel to itself, the rings are observed to appear successively at the centre and to expand and move progressively outwards, at the same time becoming closer to each other. On the other hand, the rings diminish and proceed towards the centre, disappearing there in turn eventually, when the air-film is made thinner. The circular interference fringes may also be seen by directly transmitted monochromatic light, the actual rings being then complementary, bright instead of dark at any particular place, the centre being a bright spot instead of a dark one. They are, however,

much stronger by reflected light, in which form they are generally used. Both Michelson, and Fabry and Perot, employ this principle (1), the latter terming it that of the "Étalon Interférentiel."

(2) When the two interference-producing surfaces are very slightly inclined from strict parallelism to each other, the intervening air-film being thus wedge-shaped to a scarcely perceptible extent, the light being strictly monochromatic and incident normally on the film of air in strictly parallel rays, the thickness of the air-film being small and order of interference low, parallel rectilinear and almost equidistant interference bands are seen, on looking through a telescope focussed on the reference mark made on one of the two surfaces (a millimetre scale with cross-line at right angles in the centre, engraved in the silvering in the case of one of Fabry and Perot's surfaces). These localised straight bands are parallel to the edge of the wedge, that is, to the line of intersection of the two surfaces produced. The outer surfaces are slightly inclined to the inner ones, as for (1), to eliminate their reflections. Fabry and Perot employ this principle (2) in their "Lame Étalon." It is also this same principle that underlies the author's interferometer, but one of the pair of equal wedge-plates is used exclusively to counteract the dispersion of the other essential one, and a third disc of black glass furnishes the second reflecting surface concerned in the interference (its other surface being matt); the outer surface of the essential disc of the pair being the other important surface, bearing the silver-ring reference mark, the air-film between them being wedge-shaped. When either of the surfaces is moved parallel to itself, so as to increase the thickness of the air-film, the bands move towards the thinner part of the film and edge of the wedge, and in the contrary direction when the movement of the surface renders the air-film thinner.

(3) Neither arrangement (1) nor (2) affords interference bands in white light, the two surfaces not being capable of adequately close approach to each other, white light bands being only produced when the paths are identical within half a dozen wave-lengths of light. But if one of the two essential surfaces be replaced by its image, acting equally well as a source, this image can be moved into absolute contact with the real surface, and even moved through it either way. The bands are then also seen, half a dozen or so on each side of the centre, in white light, through the telescope focussed on the real surface (the reference surface carrying the mark, a rectangular cross-hatching like squared paper in Michelson's apparatus), where the bands appear to be localised. As in (2) they are parallel to the edge of the wedge, the air-film being as in (2) minutely wedge-shaped, and all but the central band are spectrum coloured; but the central one is quite black. This black band corresponds to the line of exact equality of path of the two interfering rays. The colours of the other bands follow the order of Newton's rings seen by reflection; if the plates be silvered the silver film must be thin, otherwise the complementary colours are afforded in the flanking bands instead, and the central one is white instead of black. This principle (3) forms a specialty of Michelson's method. It is also employed by Fabry and Perot when extended to

include superposition of two étalons interferentiels one of which is of half or double the length of the other. Bands in white light are indeed afforded in general when one path is a multiple or sub-multiple of the other, but the intensity falls off with the degree of multiplication or division ; it is quite good, however, for the simplest first case, halving or doubling, and usable up to the ninth or tenth.

The two similar glass wedge-plates in methods (1) and (2) are best cut from the same large plate of truly planely worked glass 10 to 15 millimetres thick, one surface of which is inclined a few minutes out of strict parallelism to the other ; it is then certain that the slight prismatic dispersion due to the wedge-shape (that of a prism of very small angle) can be exactly counteracted by arranging the two plates contrariwise to each other as regards the direction of the wedges.

With respect to the rings and straight-line bands of methods (1) and (2) it should be remembered that the concentric rings or straight parallel bands are closer together the shorter the wave-length of the monochromatic light employed, other conditions remaining the same. Also that the straight parallel bands of method (2) are also closer together the greater is the small angle of deviation from strict parallelism of the two essential reflecting surfaces ; when the surfaces are very nearly absolutely parallel the bands become so wide that two or three, or even one only, are in the field at a time, but when the tilt is more appreciable a considerable number of parallel bands close together are afforded. The conditions are most suitable when about a dozen bands are visible in the circular field of the telescope, as shown in Fig. 891 on page 1311.

Michelson's Interferometer and its Use in Comparative Measurement.—A form of interferometer of great interest on account of the valuable uses to which it has been put by its deviser, Prof. A. A. Michelson of Chicago,[1] including the enumeration of the exact number of wave-lengths of the three cadmium radiations contained in the French standard metre at Sévres near Paris, may with propriety be briefly described here. For although it is not suitable for the specific crystallographic purposes immediately under discussion, yet for a necessary understanding of the subject of interferometry, and its considerable possibilities in further crystallographic work, it is desirable to include a brief account of the instrument, especially as it involves two additional principles to that, principle (2), of the author's interferometer, namely, the use of parallel rectilinear interference fringes in white light produced by interfering rays of exactly equal path, principle (3), and circular fringes in monochromatic light when the difference of path is greater, principle (1).

The essentials of the Michelson interferometer are shown in Fig. 906. The light from a vacuum tube *a* or other source passes through a spectroscope *bcd*, in order that monochromatic light, corresponding to one line only of the spectrum of the incandescent vapour in the vacuum tube, may be isolated and allowed to pass through the slit *d* to the interferometer. The latter consists primarily of two transparent glass

[1] A very readable account of the instrument and the results achieved with it is afforded by Prof. Michelson's book, *Light Waves and their Uses*, University of Chicago Press, 1903.

plates with truly plane and parallel surfaces e and e' inclined at 45° to the direction of the light rays, two mirrors f and g also truly plane, and quick and fine movements of great steadiness for one of the mirrors, f, parallel to itself and along the horizontal direction normal to its surface by the sliding of its carrier over a very truly constructed V-and-plane bed, and with micrometric record of the motion to 1/10,000 millimetre. The other mirror g is the "surface of reference," and is usually engraved with horizontal and vertical lines at equal intervals so as to form squares, as shown in Fig. 910. The monochromatic light from the slit d falls obliquely (at 45°) on the plate e, at the first surface of which (this surface being usually very slightly silvered) it divides, part being reflected through the second plate e' to the mirror f, and part passing through e direct to the reference mirror g; the very light silvering of e more or less equalises the intensities of the reflected and transmitted portions of the light, a condition for the production of sharp fringes. The first part is reflected at f and returns along the path $e'eh$ to the telescope h, and the second part is reflected at g back to e, from which it is reflected also into the telescope. **If the paths of the two parts,** which by the device of introducing the second plate e' have suffered the same number of reflections and refractions under identical conditions (from the first surface of e to f and back, and from the same surface of e to g and back respectively) **are exactly equal, and ordinary white light be used** instead of that from the spectroscope, **parallel rectilinear interference bands are produced** (the ordinary interference bands of thin films), and seen on looking through the telescope focussed on them (on the image of the reference surface in e). To produce these straight bands the two surfaces are not absolutely parallel, but very slightly indeed tilted with respect to each other, by the slightest touch (just adequate to produce the desirable width of band) of one of the adjusting screws. It is the virtual image of the engraved reference surface g in the silvered surface of the plate e which constitutes the true plane of reference, and it is this plane which requires to be just out of exact parallelism to the actual mirror surface f, for the production of parallel straight-line interference bands. These rectilinear bands would then be produced in monochromatic light for considerable path differences, dependent on the homogeneity of the radiation used. No bands are seen, however, in white light unless the difference of path does not exceed a very few wave-lengths, at most a dozen, of an average radiation. In focussing the image of g in e the actual surface f is also focussed, and so the effect is that of focussing the *locale* of interference bands produced by interfering rays due to the actual surface f and the image of g, acting as sources. The band which is central when the paths are precisely equal—and adjustment of the movable mirror can always bring them so—is black, and the others parallel to it on each side are

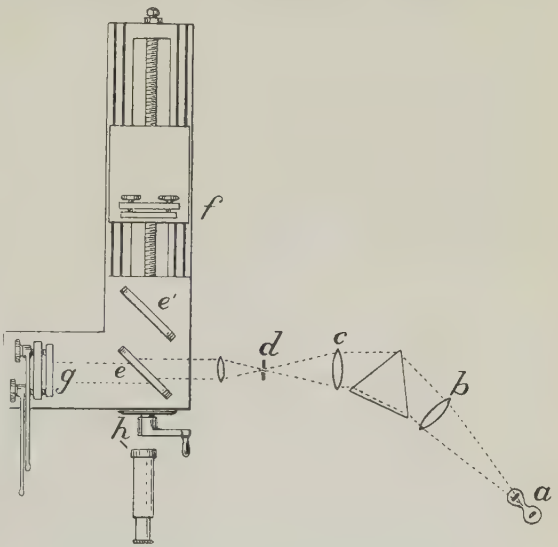


FIG. 906.—Plan of the Michelson Interferometer.

spectrum coloured and diminish progressively in intensity until after the sixth or seventh they fade away, as illustrated in either the upper or lower part of Fig. 907, the appearance being practically the same as that afforded by the Babinet compensator as shown in Fig. 838 on page 1164; hence, it is very easy to adjust for equality of path by bringing the very readily recognisable black band to the centre of the field of view of the telescope and adjusting it to the cross spider-lines, the vertical line being preferably double so that the black interference band can be adjusted between these two parallel spider-lines. It will be recognised that this is the method of principle (3).

When the surface of the mirror g is so adjusted, however, that its image in e is absolutely parallel to the surface of the movable mirror f, and the telescope is adjusted for parallel rays, spectroscopic monochromatic light being used, the interference fringes are no longer straight parallel lines but concentric circles like Newton's rings. Moreover, unlike the bands in white light, these circular fringes are not localised bands and they continue to be visible for a difference of path which may amount to a vast number of waves, in the maximum as many as somewhat over 300,000; their visibility depends on the homogeneity or otherwise of the radiation employed, exactly as in the case of the rectilinear interference bands produced by the author's interferometer. The range of visibility is only slightly more than 2 millimetres (a path of 4 mm., the journey being a return one) in the case of red hydrogen light, but is somewhat beyond a decimetre, that is, 20 centimetres of path, in the case of the very homogeneous red light of cadmium vapour, corresponding to 310,632 waves.[1] This method will be recognised as that of principle (1).

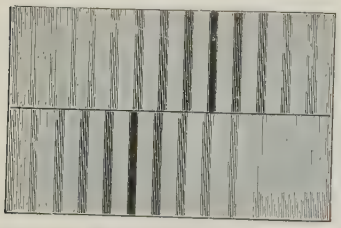


FIG. 907.—Michelson Interference Bands in White Light.

If while white light is employed and the paths of the two sets of rays from g and f are equal, the black interference band being central and upright, an extremely thin film of mica, or better still the yet thinner film of glass obtained by blowing a bulb on glass tubing until it bursts, be held in the path of one of the two sets of rays, and so as only to screen one half of the field of view of the telescope, the bands in this part of the field will be displaced from the centre to one side, as shown in Fig. 907, which reproduces the effect in the portion of the field chiefly concerned, the upper half showing the bands in their original position and the lower half showing them when displaced; and if the mica or glass film be of more than the extremest tenuity the bands will be taken right out of the field, the difference of path introduced by the film, dependent on its refractive index, being more than the dozen or so of wave-lengths, which correspond to the limit of visibility for fringes in white light. The number of waves introduced is $2(n-1)\frac{t}{\lambda}$, where n is the refractive index of the film introduced, t its thickness, and λ the wave-length of the light. For instance, a plate of one millimetre thickness, of glass of refractive index 1·5, in light of wave-length 0·0005 mm. (half a micron), will produce a difference in path of 2000 waves.

In this essential form, but with the necessary detailed modifications and refinements, Michelson used this interferometer for the evaluation of the French standard

[1] The wave-length of red cadmium light is 0·0006438 or 1/1553 millimetre or 1/39,459 inch. Michelson in the year 1892 found in the French metre 1,553,163·5 waves of red cadmium light; Benoit, Fabry, and Perot, employing the method of Fabry and Perot, in a later determination, in the year 1907, found the number to be 1,553,164·13 waves. There are thus 1553 waves in a millimetre, 15,531 in a centimetre, 155,316 in a decimetre, and 310,632 in 2 decimetres.

metre in cadmium wave-lengths, at the Bureau International des Poids et Mesures, Sévres, in the year 1892.[1] The length of a metre is obviously too great for the direct observation of interference bands afforded by two plates thus far separated, or to count the number of bands (twice that of the wave-lengths) to which such a length corresponds. For it has to be remembered that the light waves traverse the distance twice, on going and in returning, so that the total length of path would be two metres. The limit of path for band visibility has been shown to be somewhat over two decimetres, so that an intermediate standard of one decimetre (path 2 dm.) was first evaluated. The number of red cadmium light waves in this decimetre standard was found eventually to be 155,316, and the interference fringes obtained between the surfaces at this distance were wonderfully clear. It is not feasible, however, to count the large number of 310,632 bands corresponding to this length, although the last fraction of a band can be checked by direct observation. So Michelson caused to be constructed eight other sub-intermediate standards, or étalons as the French call them (a word which we have Anglicised), exactly like the decimetre

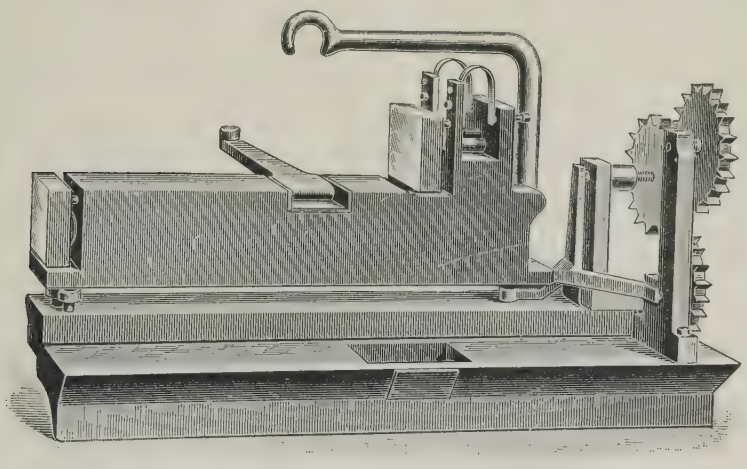


FIG. 908.—Michelson's Decimetre Étalon.

standard in construction, but each of which was half the length of the previous one in the whole series of nine ; they corresponded respectively to the numbers of fringes for red cadmium light 155,316, 77,658, 38,829, 19,414, 9707, 4853, 2426, and 1213, this last being an étalon in which the two reflecting surfaces were less than half a millimetre apart (0·3906 mm.). This number, 1213 circular fringes, can readily be counted, given the necessary patience.

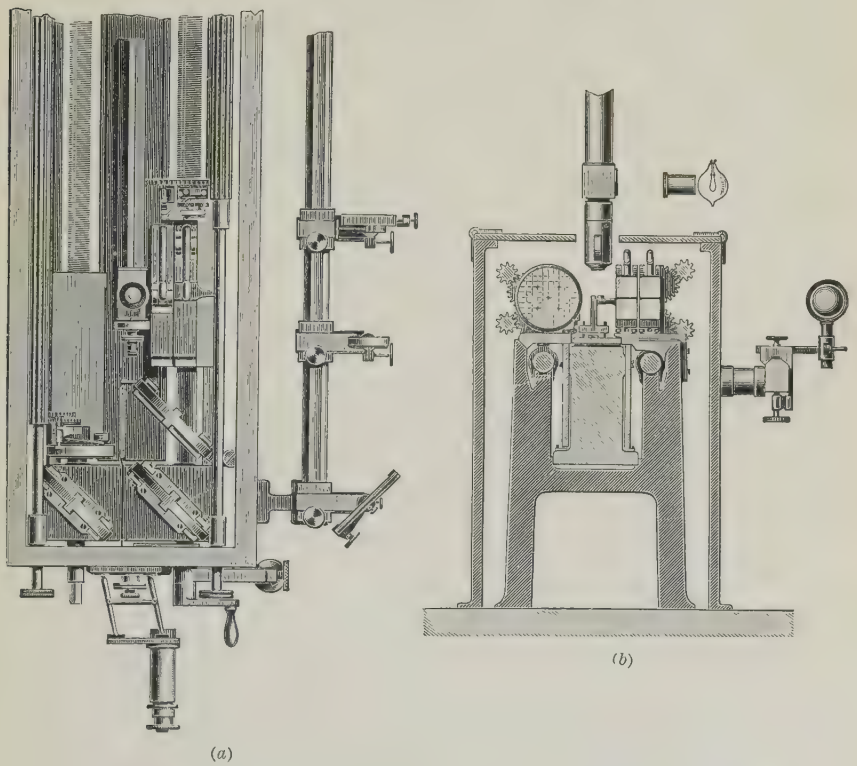
One of the étalons, the decimetre, is shown in Fig. 908. It consists essentially of a rigid metal slider (over the V-and-plane bed) carrying two vertical glass plates 2 centimetres square and nearly a centimetre thick, very truly plane-polished and silvered on the front surface ; one is fixed at the front end of the slider, and the other near the back end and at a height which brings its bottom edge on a level with the top edge of the front plate. Both plates are provided with fine adjustments to strict parallelism of the two silvered front surfaces. The normal distance between the planes of the two silvered surfaces forms the intermediate standard length, one decimetre in the case of the étalon shown in Fig. 908.

[1] *Trav. et Mém. Bur. Internat. des Poids et Mesures*, 1895, *11*, 3-85.

Now the feature of Michelson's interferometer has been shown to be the possibility of bringing the paths of the two sets of rays (which it develops for the purpose of producing their interference and consequent exhibition of fringes) to exact equality, and therefore of producing the fringes not only in monochromatic light but in white light. This is rendered possible by the fact that it is the image of one source of the rays (one of the mirror surfaces, *g* in Fig. 906) only, and not the mirror itself, which is brought to occupy the same position as the real surface (*f* in Fig. 906) acting as the other source. In cases where the two real surfaces themselves are used, as in the author's interferometer and the Fabry and Perot étalons to be referred to in the next section, the two surfaces can never achieve to actual identity, although they may get within two or three semi wave-lengths of that position, when the cushion of air between the two surfaces is removed by sliding one over the other or by working in a vacuum. But it is readily possible with Michelson's apparatus to bring two different surfaces, say the two silvered surfaces of one of his étalons when arranged in position and capable of sliding on its V-and-plane bed, to absolute identity of position, by bringing each in turn to act as *f* in Fig. 906 and afford the bands in white light in conjunction with the surface *g* (used as a reference surface) acting as the other, constant, source. In actual practice Michelson found it convenient to invert the process, and to adjust first the front silvered surface to yield the bands in white light in conjunction with the reference surface *g*, and then to leave the étalon fixed, but to move the reference mirror *g* instead backwards for a distance equal to the length of the étalon until the bands are again produced in conjunction with the back silvered surface of the étalon. As this movement of *g* to the left in Fig. 906 would make a large elbow extension of the apparatus necessary, another mirror is introduced at 45° between *g* and *e* in order that the rectilinear movement of *g* shall occur conveniently parallel to that of the étalon, on a similar V-and-plane bed alongside the other. This will be clear from a view of the apparatus from above, which affords a kind of plan, given at *a* in Fig. 909. An end view, partly in section, is also given at *b* in Fig. 909. The arrangement at *a* in Fig. 909 is exactly the same as in Fig. 906, except that there are now two V-and-plane beds for sliders, parallel to each other, and save also for the placing of *g* parallel to *f* and the introduction of the new mirror where *g* had been, but at 45° to the old position of *g*, in order to direct the rays to and from *g* in its new position. Also the single mirror *f* is now represented by the pair of étalons, one (the larger, arranged to the right) of which is fixed and the other is arranged to the left on the slider moved by the fine screw; there are only the two V-and-plane beds, one for the slider carrying the étalon to be moved, and one for the slider of the reference plane *g*, both carried parallelwise alongside each other as part of the massive basal casting. Between these two beds there is just room for the fixed carrier of the standard bar, the movable étalon being next, quite close, to the standard bar. The reference surface *g* is divided into small squares, as indicated at *b* in Fig. 909, and also in Fig. 910, by two sets of lines at right angles, for the more accurate determination of the positions of the fringes from the various étalon surfaces; and the extent of its surface is adequate for its image to cover all four étalon plates at once, each quadrant thus corresponding to the field of one étalon plate, so that white light rectilinear, or circular monochromatic, fringes in any quadrant will be known to be due to the interference of rays reflected by the reference surface and by the particular étalon visible in that quadrant. This will be clear from the three cases illustrated in Fig. 910.

The first and main operation was to determine the number of wave-lengths in the smallest (first) étalon. This was done by placing this étalon on the movable carrier on the left, and the second étalon as a fixture to the right of it, and then producing the rectilinear fringes in white light, by adjusting to absolute identity the paths from the front surface of the first étalon and from the reference surface, by the adjustment of the central black band (étalon I. being slightly inclined to the reference

plane), as afforded by the étalon surface in the lower left quadrant, to the spider-lines of the telescope. Then the reference image and front surface of étalon II. were adjusted to strict parallelism, by adjustment of étalon II., the white light was switched off and the field illuminated with red cadmium light, when the circular fringes were seen, as shown at *a* (laterally inverted, for the case when I. is on the right and II. is on the left, both arrangements being used in different determinations) in Fig. 910, being observed in the other right lower quadrant corresponding to étalon II. simultaneously adjusted alongside étalon I. The reference surface was then moved backwards with extreme slowness and steadiness, using the exceedingly fine screw movement on which immense care had been bestowed, and the rings were counted as they



(*a*) (*b*)

FIG. 909.—Michelson's Apparatus for Evaluation of the Metre in Cadmium Wave-lengths.

passed outwards from (appearing one after another at) the reference centre. Or the bands may be counted as they disappear at the centre, the reference surface being moved forwards from the second position to the first. This counting continued until the reference surface had been moved exactly through the distance corresponding to the length of the first étalon, when the bands in white light (momentarily switched on) were again produced as the image of the reference surface became coincident with the second surface of the étalon ; the counting of the cadmium bands continued until the black band produced in the upper left quadrant was absolutely centrally adjusted. The whole observation was then repeated for green cadmium light, and subsequently for the blue light of cadmium. The number of circular fringes which passed the reference centre proved to be 1212·37 for red, 1534·79 for green, and 1626·18 for blue cadmium

light. The method thus consisted in using the second étalon merely to produce the circular fringes, while the first étalon was used to produce the black band in white light and thereby to fix the coincidences of the reference surface with the two surfaces of this first étalon, the same movement of the reference surface backwards serving both purposes, and the number of circular fringes thus corresponding exactly to the interval between the two productions of the black band in white light.

After verification of these results by different observers and at different times by each, the next process was proceeded to, of comparing this étalon I. with the succeeding one, II., of double the length. The two étalons were placed as before side by side as close as possible, the larger to the right, and so that the white-light fringes could be produced by both the two front surfaces, in conjunction with the reference surface, and seen simultaneously in the field of view of the telescope, as shown at *b* in Fig. 910. The back surface of the evaluated smallest étalon I. was next made to produce the coincidence white-light bands (left upper quadrant) with the reference surface, by movement backwards for the necessary distance of the reference plane, the étalon remaining fixed ; then this étalon itself was also moved backwards, until its front surface again gave the coincidence bands ; on then moving further backwards the reference surface until the back plate of the smallest étalon again gave the bands, these white-light bands were also simultaneously seen in the right upper quadrant as given by the back surface of the larger étalon, as shown at *c* in Fig. 910 ; for the length of the latter was con-

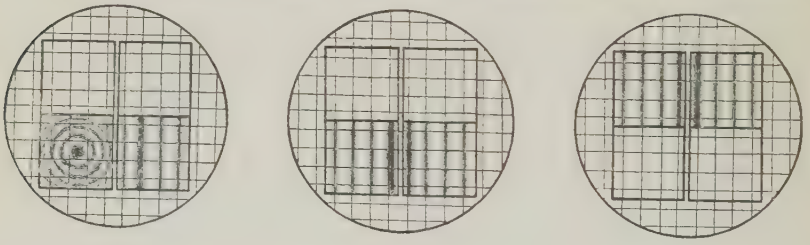


FIG. 910.—Monochromatic Circular and White Light Rectilinear Fringes, as seen with Michelson's Étalons.

structed to be as exactly as possible double that of the smallest étalon, correct within the fraction of a band. Each time, of course, careful adjustment of the central black band had been made to the spider-lines. The last fraction of the double-étalon was carefully determined, first by observing any displacement of the black band from the centre, and then by comparing the bands from the two surfaces of the étalon in monochromatic light (as seen in the upper and lower quadrants of the field, and in conjunction with the same reference surface), for the three specific radiations of cadmium, thus determining the exact number and final fraction of wave-lengths of these three radiations in this étalon. The process was repeated for the second and third, and so on for every pair up to the 8th and 9th, until the total number of wave-lengths of red, green, and blue cadmium light had been determined for the decimetre intermediate standard, and the final fraction verified and corrected by the direct observation of the bands in monochromatic light for this maximum difference of path.

The penultimate operation was then carried out, of comparing the decimetre intermediate standard with the metre. This was practically a repetition of the comparison of two consecutive étalons, except that the stepping off had to be repeated ten times. The front silvered surface of the étalon was adjusted to yield the coincidence fringes in white light with the reference surface, and the latter was then moved backwards until it gave the coincidence bands with the back surface of the étalon, then the étalon was moved back a decimetre, until its front surface again gave the bands, when the

reference surface was moved back another decimetre so as to yield coincidence once more with the back étalon surface, and so on for ten decimetres, the whole metre.

The ultimate operation was really part of the penultimate, and was performed simultaneously with the first and last adjustments of the reference surface, that is (1) with the adjustment to coincidence of its image with the first front surface of the decimetre intermediate standard, when the latter was adjusted at its first position for the beginning of the metre, and (2) with its final adjustment to coincidence of its image with the back surface of the étalon, when the latter was adjusted to its last position for the completion of the metre. The metre bar was arranged on the common massive stand which carried the whole apparatus, between the V-and-plane bed which carried the slider of the étalons and the similar bed of the reference-plane sliding carrier, as shown in Fig. 909. It bore the usual defining lines near each end. The decimetre étalon also carried an arm, as shown passing backwards horizontally in Fig. 908, having at its end a button bearing a similar defining mark. The reading microscope provided for the observation of these defining marks was arranged to be able to focus either the mark on the bar or that on the étalon, which are arranged closely side by side when in position, as clearly shown at *b* in Fig. 909; and this being done for the first and last coincidence positions as just described, enabled the final operation of comparing the étalon result with the metre as defined by its marks to be achieved.

The final result of this beautiful work of Michelson was that the French standard metre was found to contain 1,553,163·5 waves of red cadmium light, 1,966,249·7 waves of green cadmium light, and 2,083,372·1 waves of the blue cadmium radiation. This result has since been confirmed by the use of the Fabry and Perot étalons to be described in a subsequent section, the actual number found being 1,553,164·13 waves of red cadmium light.

The only weak point in this remarkable determination is in the final comparisons between the glass-plate étalons (either of Michelson or of Fabry and Perot) affording the interference fringes, and the standard metal bar itself, on which the defining lines were similar to those of the British platinum-iridium yard bar. Now the author has shown on page 1357 that the thickness of each of these scratches corresponds at least to the passage of 15 interference bands; and as the centre of the scratch has in each case to be estimated, that is, in each of the two (initial and final) comparisons, not to speak of the intervention of the observation also of the mark on the étalon arm, it will be apparent that the accuracy of the final result is not comparable with that of the purely interferential comparisons of the étalons with one another, in which every final fraction of a band could be revised and corrected by direct observation if, as usually happened, a minute correction were required. The author has suggested the removal of this final defect by the use of the fine rulings of the late Prof. Grayson, 1/40,000th of an inch apart, using five such consecutive rulings as the "location signal," of which the third, central, line of the five should be the defining line. Such a signal has already been referred to on page 1358 and illustrated in Fig. 905, the five lines being seen in the centre, parallel to the long edges of the page. Each interval between two consecutive lines corresponds to the passage of two interference bands of red cadmium light only, and the lines are so beautifully fine and clear that a very small fraction of the distance between two consecutive lines can

be accurately measured by the microscope micrometer. Such a defining mark,[1] if the suggestion were adopted, would have the same order of fineness and accuracy as the interference bands themselves, and the author has used such defining marks in many operations with the Standard Comparator described in the last section.

It should be mentioned, in concluding this reference to metrology, which has been necessary to elucidate the various methods of interferometry, that in the very latest work at the Bureau at Sévres, carried out by Dr. Guillaume,[2] the successor of M. Benôit, the low-temperature vacuum discharge through neon has replaced the hot cadmium vapour discharge

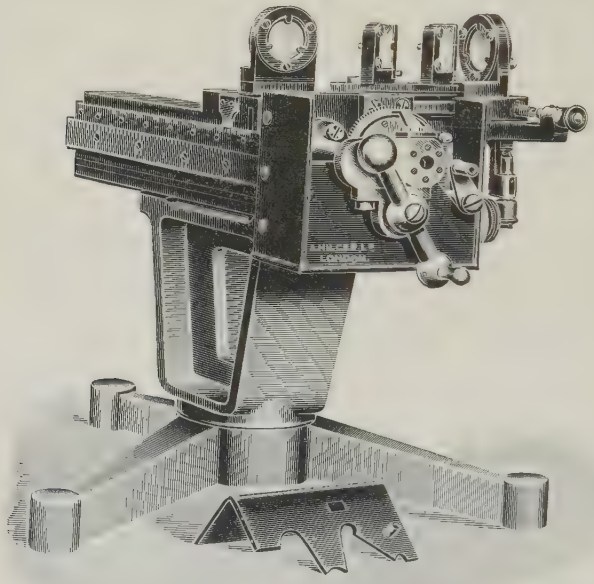


FIG. 911.—The Hilger Form of Michelson Interferometer.

as source of light, the yellow line of neon proving to be as strictly homogeneous and non-resolvable as the red line of cadmium.

An excellent form of the Michelson interferometer for experimental study of the phenomena of interference fringes, as well as for use in actual investigation, is supplied by Messrs. Hilger. In its latest form it is shown in Fig. 911.

The plates and mirrors are mounted in a finely adjustable manner on a massive stage, which in plan is very similar to Fig. 906, but with the elbow-piece to the right instead of to the left. A sliding movement is provided for the movable mirror which affords a travel of 20 centimetres, in a manner which secures great steadiness. The slides are of specially forged steel, and the sliding surfaces are worked optically flat,

[1] *Phil. Trans.*, A, 1909, *210*, 30.

[2] *Mém. Bur. Int. des Poids et Mesures*, 1917, *16* (116 pages).

so as to secure the desired accuracy in maintaining the parallelism of the movable mirror to itself in its progress from one end of the slide to the other. The slow motion mechanism is carefully covered in to avoid dust, and the screw of one millimetre pitch has not only a head divided directly into 100 divisions, but is manipulated by a slow-motion screw, the head of which is also divided into 100 parts, so that the 1/10,000th of a millimetre of motion can be read off. The carriage can be lifted off its V-and-plane bed, and automatically arranges itself in position for the action of the screw on replacement. The end of the main screw towards the observer is polished flat, and thrusts against a thick plate of polished quartz arranged perpendicularly to the axis of rotation of the screw, the other end of the screw thrusting against a fixed but adjustable screw. By directing light in the direction of the axis of the screw, through the quartz block, interference fringes can be seen as produced between the metallic and quartz surfaces, and both the closeness and the perpendicularity of the quartz to the screw axis adjusted thereby, with the aid of a system of opposing screws.

This refined instrument has proved exceedingly useful, and its usefulness has been lately enhanced by arranging that the Michelson plates and mirrors can be interchanged, if it be so desired, for the étalons of Fabry and Perot, for which the necessary fittings are provided.

The Étalon of Fabry and Perot.—The form of interferential étalon introduced by MM. Fabry and Perot conforms to principle (1) of page 1364, and consists in its simplest form of a single thick plate of glass, with truly plane and parallel surfaces, from which the monochromatic light employed is reflected, or through which it is transmitted (internal reflections occurring), and caused to produce by interference the circular fringes, best seen through a telescope adjusted for parallel rays, although they can be seen quite well by the naked eye. For when a beam of monochromatic light (say from a large sodium flame or a Cooper-Hewitt mercury lamp) is passed through two parallel surfaces of glass at normal incidence a series of alternately bright and dark concentric rings are seen on looking through the surfaces at the light. The appearance of the rings in mercury light is shown at *a* in Fig. 913. When the surfaces are those of a single plate, as in this case, the plate is used as an étalon of definite and fixed length of path, the temperature remaining constant. But the form of étalon which is most useful and is usually employed consists of two thick glass plates having truly plane-polished surfaces, one surface of each being lightly silvered, and these two silvered surfaces being those from which the reflection is to be used so as to produce interference rings. The two surfaces of either one and the same plate are not truly parallel, but inclined to each other at a few minutes angle, which is the same for each plate, in order that the secondary interference systems, caused by the interference of the reflections from the unsilvered surfaces with either of the essential reflections or with each other, may be eliminated. The plates are really cut from the same slightly wedge-shaped large plate, and are usually cut with circular peripheries rather than square. When the two plates are mounted the wedges are reversed to each other, so that the total deviation is zero. That surface of each plate which is to be the inner one (facing the silvered surface of the other plate) is silvered by cathodic deposition from freshly electrolytically deposited silver, this mode of deposition furnishing films which cause a minimum

loss of light. The plates may either be separately mounted, most conveniently on the apparatus of Messrs. Hilger described in the last section and shown in Fig. 911, instead of the Michelson plates and mirrors; or they may be supported, with the silvered surfaces nearest each other and parallel to one another, in a common mount, as shown in Fig. 912, separated at the required distance by a "distance-piece" consisting of a hollow cylinder of silica (fused quartz) placed between the plates. The coefficient of fused silica being less than that of any other known material except invar, namely, only 0·000,000,59 per 1° C., about 1/17th that of platinum, any effects due to change of temperature are negligible for all but the most refined research work. The plates are pressed against the rounded distance pieces with the aid of springs which allow a variable pressure to be applied, which enables the actual parallelism of the two important surfaces to be absolutely adjusted.

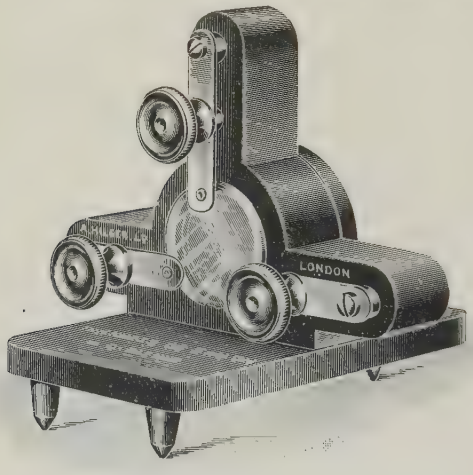


FIG. 912.—A Fabry and Perot Étalon.

The principle of the method is that slightly convergent light falls on the two lightly silvered surfaces, with air between them, in such a manner that every incident ray gives rise by the repeated internal reflections to numerous other rays of diminishing intensity. These rays are brought to interfere in the focal plane of a lens; at all points lying in a circle the same intensity prevails, so that we get a system of concentric bright and dark rings formed, which are observed in the focal plane. The difference of phase of two successive beams, or the order of interference, n, is $\frac{2d}{\lambda}$, where d is the distance between the half-silvered surfaces, that is, the length of the étalon. (This corresponds to $d = n\frac{\lambda}{2}$, the conditions in the author's interferometer. A typical field of the rings is reproduced at a in Fig. 913.

The separate mode of mounting is, of course, to be used when it is desirable to work at different thicknesses (lengths of path). But the second mode of fixed mounting in one mount has the advantage that it enables the étalon to be used on the spectroscope, placed between the objective of the collimator and the prism, as shown in Fig. 912a; a small adjustable table and the necessary space are provided on the most recent

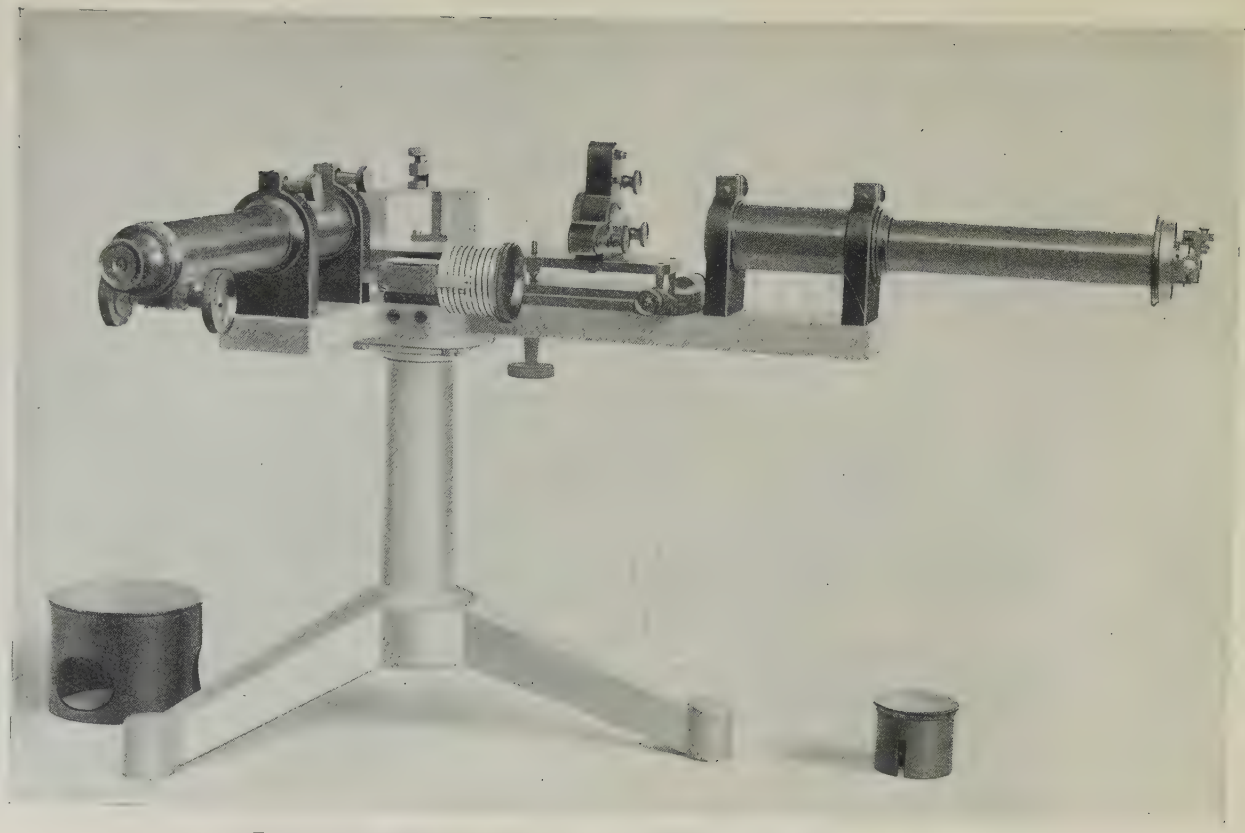


FIG. 912*a*.—Hilger Wave-length Spectroscope with Fabry and Perot Étalon in Position.

form of wave-length spectrometer supplied by Messrs. Hilger and illustrated in the figure. The interference ring system corresponding to all the brightest lines of the spectrum of an incandescent vapour (in a Geissler tube for instance), say the three principal lines of cadmium or hydrogen, or the green and yellow mercury lines, may then be studied simultaneously. For the lines of the spectrum are visible in the same positions, but not quite so bright as if the étalon were not there; each line, however, is now a strip (its apparent dimensions depending on the width of the slit and the eyepiece magnification), cut out of the interference ring system which would be produced by the étalon if the field were filled with light of the wave-length in question only; and the diameter of the ring system for each line can be measured by the micrometer eyepiece of the telescope. The appearance of the green and yellow mercury lines under these circumstances is shown at *b* in Fig. 913. That on the right is the green line 5461, and that on the left is the pair of yellow lines 5791 and 5770, which overlap owing to the slit being wide. As supplied by Hilger, the thickness of each étalon so mounted is engraved on the mount, correct to 0·005 millimetre; 7 mm. is a favourable distance *d* between the silvered surfaces, for use with green mercury light 5461 Å.U. The ring system afforded by this light under these conditions is that which is reproduced at *a* in Fig. 913. The different rings are successive spectra of the same line.

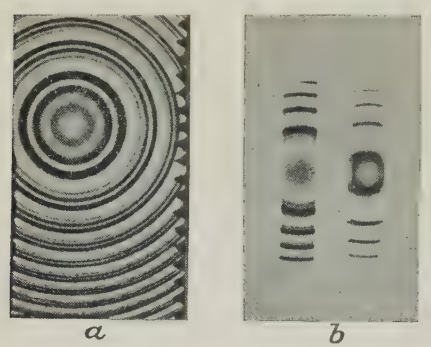


FIG. 913.—Fabry and Perot Rings in Mercury Light.

In the case of the separately mounted étalons supplied with the Hilger form of Michelson interferometer, the plate nearest the observer is fixed, but in a very finely and accurately adjustable manner, and the second plate, behind it, is carried on the slow movement platform, so that its position can be varied from all but contact with the first plate to any amount of distance of separation up to the limit (20 centimetres) of the sliding movement by the fine-motion screw. With the aid of these two forms of the étalon, and a small observation telescope with cross web for viewing the fringes also supplied by Messrs. Hilger, practically all the experiments and determinations described by MM. Fabry and Perot[1] in their various memoirs can be carried out.

A convenient arrangement is to reflect the light from a mercury lamp, by a mirror on adjustable stand, normally towards and along the axis of the étalon from behind, the beam passing on its way through a finely ground glass plate diffuser. To view the circular bands by trans-

[1] *Ann. de Chim. et de Phys.*, 1902 (7), *25*, 98, and 1904 (8), *1*, 5; *Comptes rend.*, 1904, *138*, 676 and 854; 1905, *140*, 848 and 1136; 1907, *144*, 1082.

mitted light the eye or telescope adjusted for parallel rays is placed in front of and directed normally at the étalon. To view by reflected light a clear glass plate arranged at 45° is interposed in the beam between the diffuser and the étalon, and the eye or telescope directed towards it from the side, so as to see the bands reflected in it.

The re-determination of red cadmium light wave-lengths in the French metre at the Bureau International des Poids et Mesures at Sèvres in the year 1906, by MM. Benoit (Directeur du Bureau), Fabry, et Perot,[1] was carried out with the aid of five Fabry and Perot *étalons interférentiels* (principle (1) of page 1364), of the lengths of 1 metre, 50 cm., 25 cm , 12·5 cm., and 6·25 cm., each one half of the length of the preceding one. They are shown, marked E_5, E_4, E_3, E_2, E_1 respectively in Fig. 913*a*, which

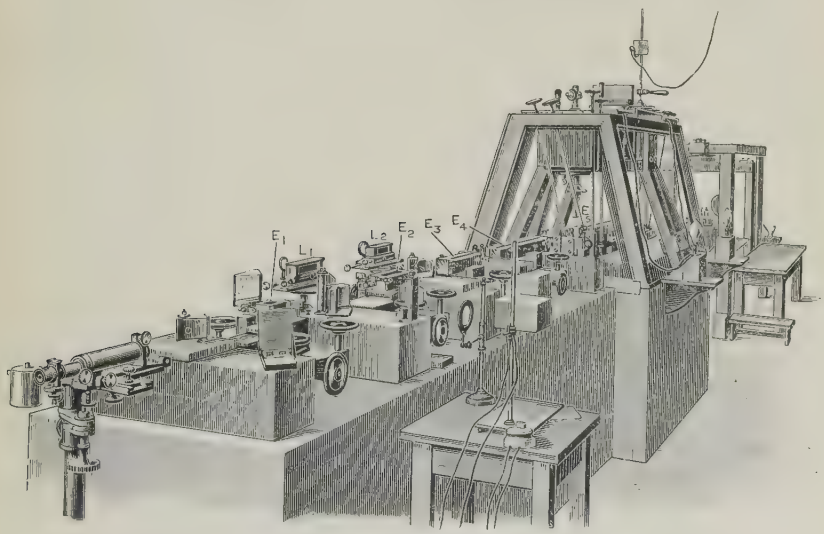


FIG 913*a*.—General View of the Fabry and Perot Apparatus for Evaluating the Metre in Wave-lengths.

affords a general view of the whole apparatus, the étalons being arranged in succession in the same straight line. Each consists of a parallel pair of thick glass plates, truly plane, of square shape, and having the inner faces facing each other slightly silvered, and kept rigidly at the desired distances by two invar (nickel steel) side-bar distance pieces, the invar having practically no thermal expansion.

The number of wave-lengths of red cadmium light contained in the length of the first étalon E_1 of 6·25 cm. was first determined, with the aid of two *lames étalons*, L_1, L_2 (principle (2) of page 1365). This étalon E_1 gave excellent circular fringes in red cadmium light, and the order of interference at the centre for the extreme length of the étalon was determined by a combination of the method of coincidences of the fringes for the three lines red, green, and blue of cadmium, and of the method of

[1] *Mém. et Trav. du Bureau Internat. des Poids et Mesures*, 1913, *15*, 1-134.

superposition of bands in white light, which latter method enabled the former to be utilised by dividing the length by five, the order of bands in this smaller length of 12·5 mm. being readily determined by coincidences, with the aid of one of the two *lames étalons* of known order of interference, whereas the whole length 6·25 cm. is too great.

The 6·25 étalon E_1 was then used to determine by the method of superposition the double number of wave-lengths in the second étalon E_2. The principle of this method is, that when a beam of white light traverses successively two plates of air with silvered faces (that is, the two plane parallel air intervals between the inner silvered surfaces of the glass plates of two étalons) a system of interference bands is obtained, visible either to the naked eye or, better, in a telescope adjusted for parallel rays, whenever the paths are either exactly equal in the two étalons, or when the path in one case is exactly a sub-multiple or a multiple of the path in the other case. Hence, these bands are produced between any one étalon and its double, used in succession in the same straight line as shown in Fig. 913*a*, the white light from a clouded electric lamp or diffused by ground glass being transmitted through both, one after the other, and in fact the second étalon can be adjusted to be exactly double by this means, or so nearly so that any slight difference can be determined by the circular fringes in monochromatic light. The bands of superposition in white light are easily produced by placing in succession a fixed étalon and an étalon arranged as an interferometer with one of its plates movable by the fine screw motion, so that the length of this étalon can be made exactly the same or a multiple or sub-multiple of the length of the fixed one, the production of the white-light bands being the indication afforded when success has been achieved. It is the principle (3) of page 1366, extended to multiples and sub-multiples of the exact length for equality of path. The centre of the system of rectilinear bands in white light, as thus seen by transmission, is a white band, when the plates are silvered, corresponding to the exact doubling or halving of the path, and it is flanked on either hand by a black band, so that two black bands in the centre of the field are the objects aimed at, and they are succeeded at similar regular intervals on each side by spectrum-coloured bands, gradually becoming feebler, the whole system of upright parallel bands filling the field. The bands become less and less clear with greater multiplication or subdivision, but are practically as good for a double or half-length as for exact equality of path. After evaluating the étalon E_2 by this means, this étalon can be used similarly to evaluate E_3, and this again to evaluate E_4, and finally the latter to determine the order of interference corresponding to E_5, the metre. The final fractions in each case are determined with accuracy by the use of the circular bands in red or green cadmium light.

The metre étalon was arranged to be 0·8 mm. less than the standard metre bar, and a fine fiducial mark was engraved on the top edge-strip of each of the end glass plates, at exactly 0·4 mm. from the edge of the silvered surface, so that the distance between these marks was the true metre. The difference of 0·8 mm. between the optical étalon and the marked metre was determined in bands of red cadmium light by an

elaborate method, in which the plates were first used as small étalons of 1 cm. and 2 cm. length between the fiducial lines, and by then determining the relations of the optical étalons constituted by the silvered surfaces in the two cases, the method of least squares being utilised to arrive at the best result from the equations of condition obtained by combination from both series of measurements. Both this determination, however, and the final comparison of the marked-metre étalon with the standard metre bar, are subject to the same defect as affects the final comparison in the case of Michelson's determination, namely, the comparative thickness of the fiducial marks, something like 15 interference bands being included in the thickness of the line.

The final results for the two methods, however, were most remarkably and satisfactorily concordant, considering this difficulty, the number of waves of red cadmium light contained in the standard metre being found by Michelson to be 1,553,163·5, and by Benoit, Fabry, and Perot 1,553,164·13. The round number 1,553,164 can thus be taken with very considerable confidence as correct.

The description of these remarkable researches of 1892–93 and 1906–7 at Sèvres have afforded a better means of making clear the principles underlying interferometry than could have been possible in any other way, and in the next, final, section of this chapter it will be shown how these principles are directly illustrated by the cleavage plates of mica crystals, and how the phenomena are affected by the crystallographic property of double refraction.

Natural Interference Rings in Mica.—Haidinger first pointed out that interference rings such as are observed, in accordance with principle (1), page 1364, between plane parallel surfaces under diffuse monochromatic light are afforded by mica, which by its very highly perfect cleavage affords thin plates with absolutely parallel faces. Lord Rayleigh in 1906 (*Phil. Mag.*, *12*, 489) also described the nature of the iris-coloured rings afforded in white light. As described in Chapter XXIX. mica is a doubly refractive substance (see page 523), the crystal system being really monoclinic, although the symmetry simulates that of the hexagonal system very closely, the crystals being almost truly hexagonal plates. But it resembles that of the rhombic system also so very nearly that the angle β between the inclined axis and the vertical axis is 90° 0′ within the very few minutes of possible error in measurement, the edge faces being usually imperfect. Moreover, the acute bisectrix of the optic axial angle lies within two degrees of the normal to the hexagonal plate, that is, within 2° of the vertical crystal axis. The crystal is very clearly biaxial, however, the optic axial angle being quite considerable, varying in different specimens of muscovite mica from 60 to 75°, as seen in air (2E). This will be clear from the photographs of the interference figure in convergent polarised light reproduced in Figs. 676 and 677 (Plate IV. opposite page 920).

In virtue of these facts, and particularly that mica is doubly refractive, there are two systems of Haidinger interference rings superposed on one another, each being due to one of the two beams polarised in planes

at right angles to each other. There are consequently regions of maxima and minima of visibility, the latter taking the form of hyperbolæ in the case of muscovite mica. These lines of minimum visibility are, in fact, practically the same as the isochromatic interference curves observed with a plate of twice the thickness in convergent polarised light. That this is so will be obvious from the reproduction of a photograph given in Fig. 914 from a memoir by T. K. Chinmayanandam,[1] who has recently made a more detailed study of the phenomena.

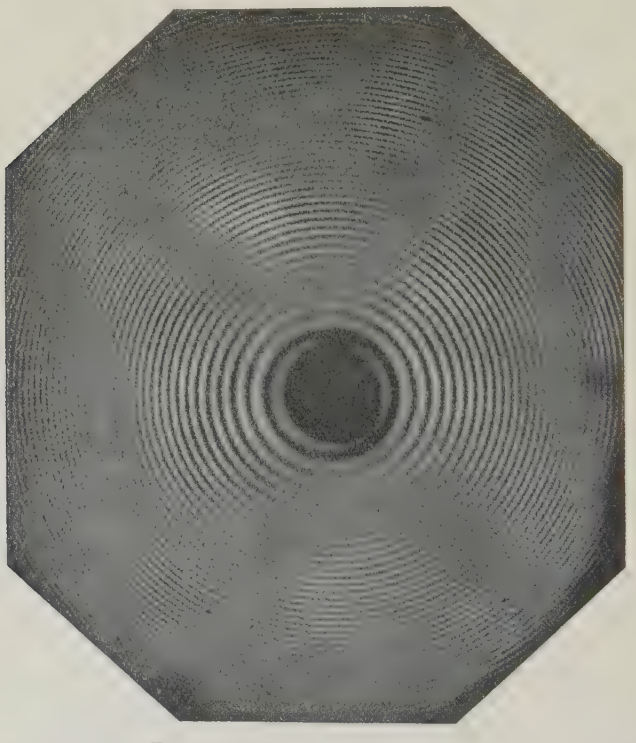


FIG. 914.—Interference Fringes of Mica.

The muscovite plate employed exhibited an apparent angle 2E of the optic axes in air of about 70°. Lord Rayleigh used a sodium flame, but this photograph was taken with the aid of a mercury lamp, provided with a suitable filter to confine the light to that corresponding to one of the mercury spectrum lines only. The plate was 0·144 mm. thick, and Lord Rayleigh used one of 0·213 mm. thickness. In order to see the rings the mica plate is simply held close to the eye, which is then directed to the mercury lamp, a ground glass plate and a green ray filter being interposed between the mica plate and the lamp in order to diffuse and monochromatise the light, when the rings and the minima curves are

[1] *Proc. Roy. Soc.*, A, 1919, *95*, 176.

clearly seen. In order to take a photograph of them a short focus lens was used, and the camera brought up so that the lens was close to the mica plate instead of the eye. But such photographs by transmitted light are not nearly as good as those by reflected light, one of which is that reproduced in Fig. 914. To obtain it a white sheet of cardboard with a small hole in the centre was held vertically in a stand, and the mica plate fixed immediately in front of it, parallel to the cardboard. The side of the latter facing the mica was then illuminated by the mercury lamp, and the rings produced by the reflected light were viewed or photographed from the other side through the hole in the cardboard and against a dark background. The back of the card and the circular edge of the hole are best blackened. For the photography the green filter used for eye vision is discarded and a cell of solution of quinine sulphate used instead, to cut off the ultra-violet rays and the two extreme violet mercury lines of 0·0004047 and 0·0004078 mm. wave-length, while leaving the bright bluish violet mercury line of 0·0004358 mm. wave-length unimpaired. The photographic action of this violet radiation is so strong that the green and yellow mercury line radiations of wave-lengths 0·0005461 and 0·0005769-0·0005790 mm. (yellow doublet) are practically without actinic influence during the time of exposure needed for violet light. An exposure of 10-15 minutes with a process plate gave the figure reproduced.

The rings are approximately two sets of ellipses corresponding to the equations

$$a^2y^2 + c^2x^2 = \text{constant, and } c^2y^2 + b^2x^2 = \text{constant,}$$

where a, b, and c are the principal velocities of light vibration in the crystal. The major axes of one set are in the same direction as the minor axes of the other.

These beautiful phenomena afforded by mica plates are thus proved to be exactly in accordance with principle (1) (page 1364) of interferometry, modified by the presence of double refraction in the film medium, which is composed of the crystal, instead of glass or air.

CHAPTER LIX

THE ELECTRICAL AND MAGNETIC PROPERTIES OF CRYSTALS

Electrical Conductivity of Crystals.—The electrical properties of conducting crystals (as distinguished from insulating crystals, dielectrics), such as those of metals, are analogous to their thermal properties as discussed in Chapter LVI. As regards electrical conductivity, cubic crystals are electrically isotropic, their electrical conductivity being the same in all directions. Optically uniaxial crystals, those of the trigonal, tetragonal, and hexagonal systems, possess a single axis of maximum or minimum electrical conductivity, and in all directions perpendicular thereto the conductivity is the converse, minimum or maximum. Hence, the electrical conductivity may be represented by an ellipsoid of revolution. In the case of optically biaxial crystals, those belonging to the rhombic, monoclinic or triclinic systems, the electrical conductivity is represented by an ellipsoid of general form, with three unequal rectangular axes. The electrical conductivity is thus different along any three perpendicular directions, and is a maximum along one of the rectangular principal axes of the ellipsoid, a minimum along another of the axes, and of an intermediate value along the third axis.

Matteucci [1] proved the rule experimentally as regards uniaxial crystals in the case of the trigonal (calcite class 21) crystals of bismuth, and Bäckström [2] confirmed this result for the case of hæmatite (specular iron ore) Fe_2O_3 crystals, which also belong to class 21. In bismuth the ratio of the electrical conductivity along the direction of the axis to that of the directions perpendicular thereto was found to be 1·6 : 1 ; in hæmatite it proved to be 1 : 1·96 at the ordinary temperature, but the value is very sensitive to change of temperature, the ratio becoming smaller as the temperature is raised. Bäckström also confirmed the rule for cubic substances by an investigation with magnetite, Fe_3O_4, which crystallises in the highest system and class of symmetry, the holohedral cubic class 32.

Good materials for determining the inner electrical conductivity in crystallised substances are difficult to find, but Bäckström was fortunate in having at his disposal some exceptionally large plates of hæmatite parallel to the basal plane {111}, exhibiting excellent well-formed plane faces of

[1] *Ann. Chim. Phys.*, 1855 [3], *43*, 467 ; *Comptes rendus*, 1856, *42*, 1133.
[2] *Öfvers. K. Vetensk.-Akad. Förh.*, 1888, No. 8, 533.

that form, bounded by smaller faces at the sides. Bars were cut from these crystals in three directions, parallel to the vertical principal axis, parallel to a lateral Bravais-Miller axis, and parallel to an intermediate lateral axis in the same equatorial plane. They were three centimetres long and of 2·5 mm. section. The end faces of the bars were first covered with copper by dipping them in a solution of copper cyanide dissolved in potassium cyanide, and then amalgamated in order to obtain trustworthy contacts. The bar was then clamped between two vertical copper springs, amalgamated on their inner side, fitted through the stopper of the heating apparatus. For temperatures under 100° C. a tin-plate vessel with double walls was used, the space between the walls being filled with water. For higher temperatures an iron vessel was used of similar design, the jacket being filled with mercury. The resistance was measured by means of a Wheatstone bridge provided with a variable resistance up to 100 ohms. As specular iron ore is strongly thermo-electrical, a Peltier effect is observed when the current is prolonged, giving a strong reverse current. The Peltier effect is just the converse of the thermo-electric effect, and occurs when an electric current from a battery is sent through the couple, thereby causing heating or cooling according to the direction in which the current passes. Hence, only feeble and intermittent currents were employed, which also enabled any perceptible heating effect by the current to be avoided.

The results showed clearly that the resistance to the passage of the current is equal in all directions in the principal symmetry plane, and that the resistance along the axis is almost twice as great as in that equatorial plane. The actual results, uniformly reduced as for a bar one centimetre long and one square millimetre in section, are as under for the three temperatures of the experiments.

Temperature.	Resistance in Ohms.		Ratio.
	Parallel to Axis.	Perpendicular to Axis.	
0°	80·8	40·8	1·98 : 1
17°	68·7	35·1	1·96 : 1
100°	33·1	18·3	1·81 : 1

The ratio thus diminished with increasing temperature, just as for all metals except bismuth. The results also show that hæmatite is quite a good electrical conductor.

In the case of magnetite, Fe_3O_4, Bäckström used a large crystal from which he prepared two bars, one parallel to the cube edges, and the other to a diagonal of the cube. They were 7·5 mm. long and 0·5 mm. in section. The resistance diminished slowly with rising temperature, and at 40° was reduced by half an ohm. The results completely confirmed the conclusion already made in earlier experiments by S. P. Thompson that the resistance is equal in all directions and diminishes with rising temperature.

Thermo-electricity.—As regards thermo-electrical effect in such metallic or other well-conducting crystals, it is in general also a function of the direction, so that two plates or rods cut from the same crystal, which is not of cubic symmetry, in different directions behave as if they were composed of two different substances, yielding, on heating the parts in contact, a current across the junction just like two different metals. No such current, however, is afforded by two differently orientated pieces of a cubic crystal, copper for instance. This was definitely proved by Bäckström [1] for plates and bars parallel to the cube and octahedron faces of cobaltite, CoAsS. If one warms a piece of a cubic crystal in contact with a similar piece of a crystal of one of the optically and thermally uniaxial systems, a thermo-electric current is obtained, and is of different strength according as to whether the direction in which the piece of the uniaxial crystal is cut is parallel to or perpendicular to the singular axis. In the case of a conducting crystal of the optically or thermally biaxial type, if two differently orientated faces of such a crystal are touched successively by a piece of a metal intermediate in the thermo-electric series between the values corresponding to the two faces, the contact with one face will on warming give a current in one direction (say positive), and that with the other face will afford a current in the opposite (negative) direction.

These facts have been experimentally elucidated by Svanberg,[2] Franz,[3] Bäckström,[1] Perrot,[4] and Marbach.[5] Svanberg showed that in the case of the trigonal crystals of bismuth and antimony, both of which cleave very readily parallel to the basal plane $c\{111\}$, bars parallel to the cleavage direction and perpendicular to the trigonal and optic axis behaved thermo-electrically more positively, and bars parallel to the axis more negatively, than any other bars of these metals. Also the thermo-electric current afforded by the two kinds of bismuth bars, or by the two differently cut antimony bars, was of considerable strength.

Bäckström studied the thermo-electricity of hæmatite with the same magnificent specimens as were used for the electrical conductivity. Two boxes constructed of copper foil were attached to two wooden discs, the upper of which was movable by means of a screw, and the crystal bar was laid between the boxes, good contact being attained by means of the screw. Through the upper box steam at 100° was blown, and through the lower box ordinary cold water was led, in which a thermometer was immersed. To each box a copper wire was soldered, and connected to a Lippmann capillary electrometer as soon as the boxes had attained a constant temperature, the thermo-electric power being directly measured in volts. The following results were obtained for the passage of the current in the directions stated :

[1] *Öfvers. K. Vetensk.-Akad. Förh.*, 1888, No. 8, 553.
[2] *Comptes rend.*, 1850, *31*, 250 ; *Pogg. Ann.*, 1853, *3*, 153.
[3] *Pogg. Ann.*, 1851, *83*, 374, and 1852, *85*, 388.
[4] *Arch. Sci. phys. et nat. Genève*, 1898, *6*, 105 and 220.
[5] *Compt. rend.*, 1857, *45*, 705.

	Volt per 1° C.
From the basal plane, perp. to the axis, to the copper	0·0002879
From any face parallel to the axis, to the copper	0·0003138
From any face of the prism zone, to the basal plane	0·0000259
From any intermediate face, to the copper	0·0002923
Calculated value for last case, from equation to ellipse	0·0002928

Hence, it will be clear that the thermo-electric power in different directions of crystals possessing a single principal axis, such as the trigonal crystals of hæmatite, is expressed by the *radii vectores* of a rotation ellipsoid.

Perrot's researches are also of special interest, as he had at his disposal some large and very homogeneous prisms of bismuth, which is the metal most easily obtained in good and sufficiently large crystals. It will be remembered that the crystals of bismuth are trigonal, with basal plane cleavage {111} or {0001}. But the metal has a very low point of fusion, so that it has only been possible to study its thermo-electrical properties up to 100° C.

Rectangular parallelepipedal blocks were prepared out of four large crystals, having faces parallel and perpendicular respectively to the axis. The largest was 30 by 18 by 18 mm. in size. The method of carrying out the experiments with them was as follows. The bismuth block was placed with its lower face resting on a thick plate of copper, *c* in Fig. 915, which had two prolongations bent over like a horse-shoe, and plunged vertically into a large vessel full of cold water. On the upper face of the bismuth block rested the copper bottom of a little metallic box *b* traversed by a current of hot water. The junctions were thus simple contacts of bismuth and copper maintained at two different temperatures. Good contact was achieved by means of a press formed by a vertically arranged bronze horse-shoe, of which the two branches (ends upwards) were spanned by a steel cap, through which the pressure screw was tapped. Two blocks of lead were arranged to slide in grooves within the horse-shoe, the lower one filling up the bottom of the shoe and the upper one *a* moving up and down with the screw, being loosely attached to a steel plate forming the lower end of the screw. Below the upper leaden block a movable one of ebonite was placed, which was hollowed out below to a shape fitting the top of the copper box *b*. The latter carried two tubes for the delivery and exit of the hot water. The plate of copper *c* was also fitted in a block of ebonite in order to insulate it from the lower leaden block. All these parts were capable of a certain amount of play, and could be loosened or tightened together by means of the screw, in order to render the bismuth-copper contact a more or less perfect one, appreciable compression being as far as possible avoided, the screw only being worked by means of its handle until resistance began to be met with. Two wires were soldered at the planes of junction, and two others led into two little water reservoirs provided with thermometers, so that the temperature of the water could be varied and recorded until the galvanometer was again brought to its zero; the two temperatures t and t' at the planes of contact, and the thermo-electric current generated, could

thus be measured, the former by the water reservoir thermometers, and the latter by means of the galvanometer, potentiometer, and a Gouy étalon of 1·386 volts at 18°.

The results of the determinations of the electromotive force for temperatures between 10° and 100° C. were as under:

The electromotive force *per* degree of difference of temperature of the two bismuth-copper contacts, that is, the thermo-electric power, was

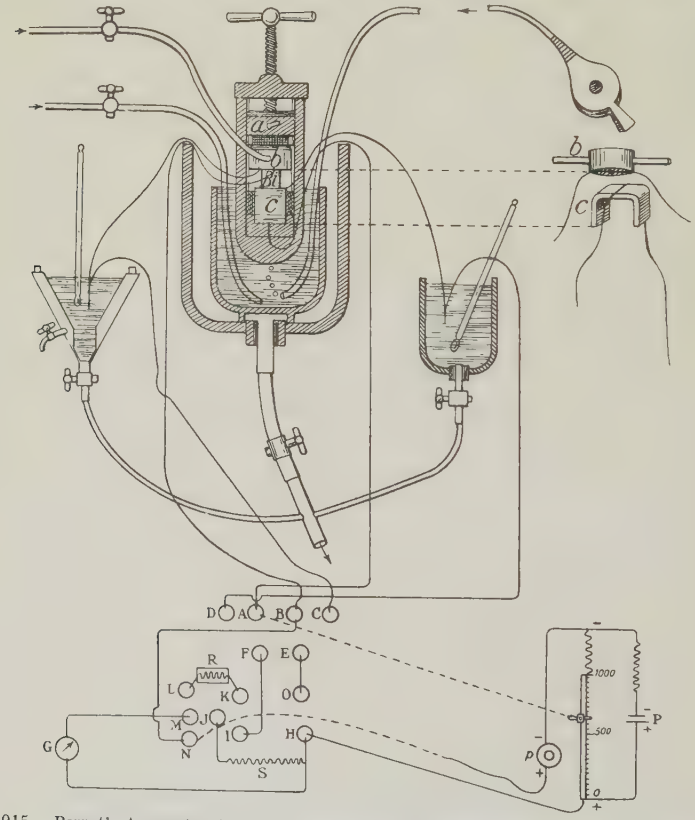


FIG. 915.—Perrot's Apparatus for the Determination of Thermo-electric Power of Bismuth in Contact with Copper.

found to increase with the temperature between 10° and 100°, and the increase was more rapid for junctions with surfaces perpendicular to the cleavage planes of the bismuth crystals (parallel to the axis therefore) than for junctions parallel to the cleavage (and perpendicular to the axis). Hence the ratio of the electromotive force parallel to the axis, to that perpendicular to the axis, becomes less as $t+t'$ increases. At 20° the ratio varied from 2·33 to 2·51, at 40° from 2·16 to 2·49, and at 100° from 1·85 to 2·10, for the four different bismuth blocks employed. The absolute electromotive force also varied for the different crystals,

for junctions parallel to the cleavage from 0·00831 to 0·01057 volt, and for junctions perpendicular to the cleavage from 0·00451 to 0·00525 volt. The differences appear to have been due to slight lack of homogeneity in the large crystals employed.

Marbach observed a very remarkable fact with respect to iron pyrites, FeS_2, which crystallises in the cubic class 30 (see page 164). It is often found in actual experiments that the rules already stated are apparently materially departed from, owing to the altogether unexpectedly large disturbing effect of minute quantities of foreign enclosures, which are so common in mineral crystals, and which often generate a current in the opposite direction to that produced by the pure substance of the crystal. Even more pronounced, however, are the apparent deviations when a mineral exists in two forms like quartz, currents of opposite characters and of equal strengths being generated by the two varieties. Now the very abundant mineral pyrites commonly displays the positive pentagonal dodecahedron {210} (this pentagonal dodecahedron being indeed often termed in consequence the pyritohedron), the negative form {120} being much more rarely developed by the mineral. These two different complementary pyritohedra develop respectively positive and negative thermo-electrical properties, the current flowing from the copper contact (the copper wire in contact with the crystal) to the crystal in the former case, and from the crystal to the copper in the other, as already described on page 164. Cobaltite, CoAsS, which much resembles pyrites and belongs also to class 30 (a crystal having been completely worked through in Chapter XI.), behaves similarly. Marbach found, indeed, that a pyrites crystal of the first kind (showing {210}) in combination with one of the second kind (showing {120}) actually produced a stronger thermo-electric current than that afforded by antimony and bismuth, the two extreme members of the thermo-electric series of metals. For it will be remembered that when the metallic elements are arranged in order according to their thermo-electric constants, antimony occupies one end and bismuth the other end of the list, and that the thermo-electric current produced at the same temperature is proportional to the degree of separation in the list of the two metals which are employed in contact as a thermo-electric couple. It must be obvious, therefore, that in this especially interesting case of pyrites the opposite or complementary nature of the crystal structure, that is, the symmetrically opposite arrangement of the metallic atoms in the two structures, is the cause of the very strongly opposite character of the thermo-electrical phenomena exhibited.

The thermo-electric list in the correct order for the mean temperature of 50° C. is : (1) antimony, (2) iron, (3) zinc, (4) silver, (5) tin, (6) copper, (7) platinum, (8) lead, (9) nickel, (10) bismuth. The rule is that if wires of any two of them are joined together to form a complete circuit, and one of the two junctions be heated, the thermo-electric current will go, in the metal which comes first in this list, from the hot junction to the cold one. Or if a compound bar be made by joining two small bars together, one end of one bar to one end of the other bar (the two simple bars being of two different metals in the list), say by soldering, and if the remaining

free ends of the two simple bars be connected by a conducting wire, a current will pass on heating the soldered junction, and will travel across the heated junction in the direction from the metal nearer to the bismuth end of the list to the metal nearer the antimony end. Thus in the bismuth-antimony couple, it moves from bismuth to antimony. Outside, in the connecting wire, which may have an indicating galvanometer introduced in its length, the current passes from the metal on the antimony side to the metal on the bismuth side. The order of the metals varies somewhat with the temperature, as thermo-electric power varies with temperature. Indeed for a specific temperature for any couple there is a neutral point beyond which reversal of the phenomena occurs.

In English text-books it is customary to treat the bismuth end of the series as the positive end, and the antimony end as negative. But the contrary is the case with German text-books. Thus, for instance, von Groth states, at the commencement of the section on Thermoelektricität in his *Physikalische Krystallographie*, that that one of the two metals is designated as positive towards which the current moves when the junction is heated, and this particular metal in the case of the extreme bismuth-antimony couple we know to be antimony, which in our text-books is considered as negative. Likewise Liebisch (pages 173 and 174 of *Phys. Kryst.*) refers to the antimony side of the thermo-electrical series as the positive side, and the bismuth side as the negative one. It is well to remember this fact, as otherwise misleading impressions will be gained. Thus the designation by Marbach of the pentagonal dodecahedron of pyrites {210} as thermo-electrically positive, and the complementary form {120} as negative, follows the German custom.

Electrical Properties of Non-conducting Crystals.—In the case of non-conducting crystallised substances, instead of variation of conductivity we have the phenomenon of variation in the value of the dielectric constant; this latter is the measure of insulation or of lack of conductivity, and of the power of preserving and accumulating an electric charge on the surface of the substance. Doubly refractive crystals which are classified with non-conductors take greater electrification in certain directions than in others, and these directions correspond to the principal axes of the optical ellipsoid; in the case of an optically uniaxial crystal the singular axis and directions perpendicular thereto take the limiting amounts (maximum or minimum) of electrification, and in the case of a biaxial crystal one of the three principal axes takes the maximum, another the minimum, and the third an intermediate amount of electrification.

It has been shown in the development of Clerk-Maxwell's electromagnetic theory of light, that the measure of the strength of the excitation, the dielectric constant, ϵ, is proportional to the square of the constant A in the well-known formula of Cauchy for the dispersion of the light spectrum, the general formula for the refractive index for all wave-lengths of light (see page 819):

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ldots$$

that is, to the square of the refractive index for a ray of infinite wave-length (for when $\lambda = \infty$ the second and third terms of the equation disappear). Hence, as the refractive index varies with the direction in the well-known manner, fully discussed in Chapter XLI., represented by the optical indicatrix ellipsoid of Fletcher (see page 876), in all but cubic crystals (for which the ellipsoid becomes a sphere), the dielectric constant, representing the power of electrical excitation, varies in like manner, but in different degree, corresponding to the square of the refractive index A for a ray of infinite wave-length. In crystals of the rhombic, monoclinic and triclinic systems the dielectric constant is thus represented by a triaxial ellipsoid. The three axes of this ellipsoid are coincident with the three crystallographic axes in the case of a rhombic crystal, and one axis of the ellipsoid is coincident with the symmetry axis of a monoclinic crystal; but in the general triclinic case none of the axes of the ellipsoid are identical with the crystallographic axes. Analogously as regards uniaxial crystals, the dielectric constant is represented by an ellipsoid of revolution in the cases of trigonal, tetragonal, and hexagonal crystals, the singular axis of which coincides with the trigonal, tetragonal, or hexagonal axis of symmetry and with the single optic axis.

Sulphur is an almost perfect insulator, and as the result of a careful investigation with some fine rhombic crystals of this element Boltzmann [1] has shown that the above rule, so far as rhombic crystals are concerned, is absolutely fulfilled, both as regards the actual values of the dielectric constant and their relative values for different directions within the crystal.

The values of the dielectric constant ϵ for the three axial directions α, β, γ of the optical and electrical ellipsoids of sulphur, identical in direction with the three rhombic crystallographic axes, as found experimentally by Boltzmann, are given in the following table, and compared with the values of A^2 calculated from the knowledge of the refractive indices as determined by Schrauf and the assumption of the truth of Maxwell's electromagnetic theory of light:

DIELECTRIC CONSTANTS OF RHOMBIC SULPHUR CRYSTALS.

Observed Value of ϵ.	Calculated Value of A^2.
$\epsilon_\alpha = 3{\cdot}811$	$A_\alpha{}^2 = 3{\cdot}591$
$\epsilon_\beta = 3{\cdot}970$	$A_\beta{}^2 = 3{\cdot}886$
$\epsilon_\gamma = 4{\cdot}773$	$A_\gamma{}^2 = 4{\cdot}596$

Considering the difficulty of such experiments, and the fact that different methods afford somewhat different results, especially when the times of duration are different, owing to the well-known absorption or "soaking-in" of electric charges on dielectric surfaces, these results are in satisfactorily good accordance.

Quite recently (1919) R. Fellinger [2] has determined the values of the dielectric constants for the axial directions of some precious stones,

[1] *Sitzungsber. Wien. Akad.*, 1874, *70* (2), 342.
[2] *Ann. de Phys.*, 1919, *60*, 181.

including topaz (colourless, from Japan), beryl (aquamarine, from Madagascar), ruby (from Siam), and sapphire (colourless, from Ceylon). He found a very marked difference between the values for the axial direction and directions perpendicular thereto in the cases of the hexagonal beryl and trigonal ruby and sapphire, but not so great a difference for the three rectangular axial directions *a*, *b*, *c* of the rhombic topaz. The constants for the two alumina (corundum) gems, ruby and sapphire, were almost identical and very high. The actual results were as follows :

Dielectric Constants of

Topaz .	$\epsilon_a = 6{\cdot}251$	$\epsilon_b = 6{\cdot}536$	$\epsilon_c = 6{\cdot}441$
Beryl .	$\epsilon_{\text{par. axis}} = 6{\cdot}076$		$\epsilon_{\text{perp. axis}} = 7{\cdot}023$
Ruby .	$\epsilon_{\text{par. axis}} = 11{\cdot}284$		$\epsilon_{\text{perp. axis}} = 13{\cdot}266$
Sapphire	$\epsilon_{\text{par. axis}} = 11{\cdot}418$		$\epsilon_{\text{perp. axis}} = 13{\cdot}186$

Pure crystals are essential in such investigations, however, for the results are bound to be materially affected by enclosures of electrically conducting foreign substances, especially liquid cavities, which destroy the perfection with which the pure substance acts as an insulator. Among substances obtainable in quantity sulphur is exceptionally perfect as a dielectric, most other substances classed as bad conductors of electricity being to a more or less slight extent conductors. J. Hopkinson's [1] well-known determinations of the dielectric constants of various kinds of glass yielded values ranging from 6·5 to 10·1, the denser optical glasses having the higher values. For mica the values obtained varied from 5·5 to 8. These values now given for the dielectric constants of crystals and glasses may finally be compared with the values as determined by Gordon for other well-known dielectrics. Thus ebonite gave the value 2·284, guttapercha 2·462, indiarubber 2·497, and shellac 2·74. Dry air is the standard, with a dielectric constant 1·00. Hence the absolute values of the dielectric constant vary very considerably in different substances, but their relations for different directions in the same crystallised substance are such as follow the above rules, which are imposed by the crystallographic symmetry.

The accumulation of electric charges on the surface of badly electrically conducting crystals must also obviously be dependent on these rules governing the dielectric constant. Some interesting results concerning this aspect of the subject have been obtained by Wiedemann [2] and de Senarmont [3] with doubly refracting crystals, as regards the degree of free surface conduction of insulating crystals. The superficial conduction was found to be proportional to the dielectric constant; for the conduction varies for different directions in the surface, being greatest for the direction in which the dielectric constant is a maximum. When an electrified vertically suspended and insulated sewing needle was brought over the plane surface of a plate of glass or resin, on which lycopodium powder (which is also a bad conductor) had been scattered, the latter was repelled until a circular patch of the glass or resin surface,

[1] *Phil. Mag.*, 1882, *13*, 242. [2] *Pogg. Ann.*, 1849, *76*, 404, and *77*, 534.
[3] *Ann. Chim. Phys.*, 1850, *28*, 257.

centred around the needle point, had been cleared of the powder. On substituting a crystal plate for the glass or resin, the portion of the surface cleared was in general elliptical in shape, the major and minor axes of the ellipse having a definite relation to the crystal structure. For instance, with isotropic (cubic) crystals the cleared space was always circular; but if the plate were one of a uniaxial crystal, cut parallel to the optic axis, the clear patch was elliptical and one of the two principal axes of the ellipse would be parallel to the optic axis, and the other perpendicular thereto. If the plate were cut perpendicular to the axis, the clearing had a circular boundary. Indeed the phenomena were exactly comparable to those observed with regard to thermal conductivity described in Chapter LVI. De Senarmont also observed the remarkable fact that when the experiment was conducted in the dark, under reduced atmospheric pressure, glowing light-figures were produced, of circular or elliptical shape according to the nature of the symmetry of the crystal and the character of the particular face on which the experiment was performed.

Pyro-electricity.—It will have been clear that the whole of the interesting electrical properties of crystals are functions of the crystal symmetry, and so far as they have yet been referred to (with the exception of the remarkable thermo-electric properties of the two complementary pyritohedra of pyrites or cobaltite) of the system of symmetry; that is, they depend on whether the crystal be cubic, uniaxial (trigonal, tetragonal, or hexagonal), or biaxial (rhombic, monoclinic, or triclinic). But besides these phenomena, which do not distinguish the holohedral class of any system from the other classes of lower symmetry within the system, there is yet to be considered the more particularly discriminating and highly interesting phenomenon of pyro-electricity—the development of opposite electric polarity in different portions of the same crystal on altering the temperature of the crystal—which is exhibited by certain crystalline substances belonging to those classes of lower than holohedral symmetry which are distinguished by a polar character, due to the possession of an axis of symmetry without a plane of symmetry perpendicular to it. It has been shown, in the descriptions of these classes of symmetry, that the two terminations of the prismatic crystals belonging to these classes usually exhibit different facial forms, and are consequently quite unsymmetrical to each other.

Tourmaline, which belongs to the ditrigonal polar class 20 of the trigonal system, as described on page 348 and illustrated in Fig. 300, is an excellent example, the long prisms having quite different kinds of faces developed at their two ends. Now, whenever such a crystal is subjected to a change of temperature electrical charges of opposite sign are developed at the two ends, the terminations of the polar axis of symmetry, which may be said to be also the electrical axis. As the temperature rises (the heating being most regularly brought about by heating in an air bath) one end of the crystal becomes positively electrified and the other end negatively, while during cooling charges of the reversed signs are developed. That end which develops a positive charge during warming and a negative charge on cooling is termed the "analogous" pole, while the other end

which develops negative electrification during heating and positive on cooling is called the "antilogous" pole. The substance being a bad conductor of electricity, the statical charges accumulate about the two ends. This may be readily demonstrated by dusting a little of Kundt's powder, a mixture of red lead (Pb_3O_4) and sulphur, from a muslin bag over the crystal, when the particles of sulphur, which are rendered negatively charged by friction with the meshes of the muslin and with the other particles, adhere to the positively electrified end of the crystal, while the particles of red lead, which are positively charged when they leave the bag, attach themselves to the other end of the crystal which had developed the negative pyro-electrical charge, the two powdered substances obviously becoming attracted to those parts of the crystal which are charged with the opposite kind of electricity to that which they themselves carry. If the dusting with Kundt's powder occurred on a crystal rising in temperature, and the charges were then removed to earth, the reverse would be found to occur on allowing the temperature to fall again, the end which on warming became negatively electrified being shown, on again dusting with the powder, to have now developed a positive charge, and *vice versa*. Fig. 916 shows this effect in the case of a typical crystal of tourmaline, the lightly dotted part representing that to which the sulphur is attached, and the more strongly dotted part that to which the red lead has adhered.

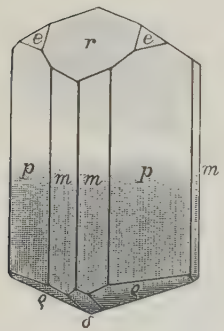


FIG. 916. — A Cooling Crystal of Tourmaline dusted with Kundt's Powder.

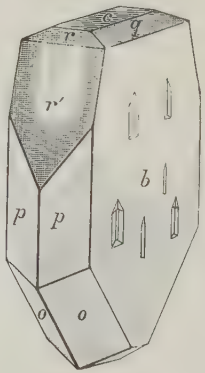


FIG. 917. — A Cooling Crystal of Hemimorphite dusted with Kundt's Powder.

Another mineral which exhibits the property of pyro-electricity in a high degree is hemimorphite, zinc silicate, $Zn_2SiO_3(OH)_2$, which forms excellent crystals belonging to the polar class 7 of the rhombic system. A drawing of a typical crystal has already been given in Fig. 190 on page 228, together with a description of the forms at the two ends, and of the analogous or antilogous character of the pyro-electricity which they develop on change of temperature. Fig. 917 will render the distribution clear. Hemimorphite is frequently referred to as "electric calamine" (calamine being the natural carbonate of zinc, $ZnCO_3$), on account of its pronounced display of pyro-electricity. In the cases of both tourmaline and hemimorphite the more acute termination of the crystal is usually the antilogous pole, becoming negatively charged on warming.

The two varieties of tartaric acid (monoclinic, of the digonal polar class 4), described on page 255 and illustrated in Figs. 211 and 212, also have a polar electrical axis, the symmetry axis, and the opposite mode of

distribution of the sulphur and red lead at the two ends of the lateral digonal polar axis of symmetry of a pair of typical crystals of the two varieties is represented at *a* and *b* in Fig. 918.

Many other substances belonging to classes of lower than the full holohedral symmetry of their system, while not polar in the same sense (exhibiting a singular polar axis) as the classes 4 and 20, still show the so-called pyro-electricity. One of the most familiar is quartz, a hexagonal plate of which, cut perpendicular to the axis, shows on change of temperature alternately positive and negative electrification at the six corners of the plate on heating or cooling, as shown in Fig. 919.

In this case it is because the three digonal horizontal axes of symmetry present in the quartz class 18 of the trigonal system are in reality each separately polar, one end of each developing one variety of electricity and the other end the opposite variety.

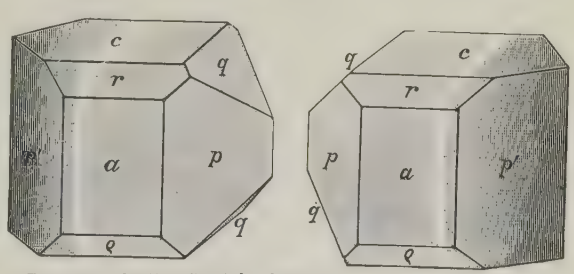


FIG. 918.—Cooling Crystals of Dextro and Lævo Tartaric Acid dusted with Kundt's Powder.

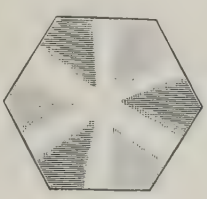


FIG. 919.—A Cooling Plate of Quartz dusted with Kundt's Powder.

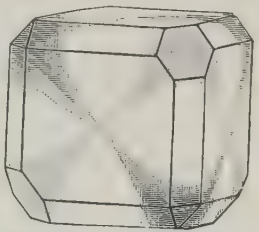


FIG. 920.—A Cooling Crystal of Boracite dusted with Kundt's Powder.

Similarly boracite, which crystallises in class 31 of the cubic system the hexakis-tetrahedral class, ditesseral polar, develops with change of temperature negative electricity on four alternate corners of the cube, and positive charges on the other four corners, as illustrated by a typical crystal in Fig. 920, the two sets of four corresponding to the two complementary tetrahedra characteristic of this class 31 of the cubic system. The four trigonal axes, the cube diagonals, are in this case four polar electrical axes, the opposite ends of each of these axes developing opposite polarity.

Piezo-electricity.—It has now been shown that, in general, change of temperature of a crystal is accompanied by a change of volume, and also that change of temperature provokes electrical effects in crystals of polar-class symmetry. It is not surprising, therefore, that if the volume be changed by the application of extraneous pressure greater than the ordinary atmospheric, or of tension, a similar electrical effect occurs to that which is provoked by change of temperature. For when the crystal is compressed, electrical polarity is observed to be produced along the electrical axis or axes, and when the pressure is removed, or tension is applied,

electrical excitation of the opposite sign is invoked. This phenomenon is termed "piezo-electricity" (from πιέζω to oppress or compress). Tourmaline and quartz, and also Rochelle salt, exhibit the phenomenon very clearly, in a manner corresponding exactly to their pyro-electrical manifestations. The fact was first observed by J. and P. Curie.[1]

Hence, pyro-electricity and piezo-electricity practically deal with the same physical facts referred to under different names. Piezo-electricity is caused by subjecting the crystal to mechanical compression or tension, whilst in the case of pyro-electricity this strain is caused through the agency of heat.

The simplest method of observing the phenomena is to place a slice of crystal, cut perpendicularly to the electric axis, between two tinfoil slabs, and to place the set between the insulated jaws of a press, one armature being connected to earth and the other to the needle of a quadrant electrometer which has its opposite pairs of quadrants connected to a cell. The signs of the charges are reversed when the press is released, or when an actual tension is effected. In agreement with the pyro-electric cases of cooling crystals shown in Figs. 916, 917, and 918, the more pointed end of the crystal usually develops positive electrical excitation on contraction.

In the case of tourmaline, when a prism parallel to the axis is taken and two end faces are ground perpendicular to the axis, and the crystal prism standing with one flat end on a solid basal support is then subjected to compression by a weight placed on the upper flat ground end, that same end which became positively electrified when the crystal was allowed to cool after heating now also develops a positive charge. On discharging and then releasing the pressure, a negative charge is developed at that same end, just as when the crystal was warmed.

In the case of quartz, when a plate perpendicular to the axis is compressed along one of the three horizontal electrical axes (from two opposite corners of the hexagonal plate), positive electricity is developed at one end and negative electricity at the other end of that axis, and also the six corners of the plate exhibit alternately positive and negative charges. The opposite conditions are developed if the compression be effected perpendicularly to one of the electrical axes. Röntgen,[2] in the course of some piezo-electrical experiments with a sphere of quartz, found that if the compression were effected along the direction of the optic axis no electrical effect was discernible at the termini of this axis, but a feeble electric charge was developed at the poles of each of the three electrical axes perpendicular to the optic axis. When the compression was applied in a direction inclined to the optic axis, and in a principal section perpendicular to one of the three horizontal electrical axes, electric charges of a moderate intensity were developed at the ends of that axis, the signs being the opposite of those observed when that axis itself was compressed. When the compression was actually effected along the direction of an electrical axis, the charges at the two ends of the axis were of the maximum

[1] *Compt. rend.*, 1880, *91*, 294 and 383; also 1881, *92*, 186 and 350.
[2] *Ann. der Physik*, N.F., 1883, *19*, 513.

intensity observed in any of these experiments of Röntgen with the quartz sphere.

It is interesting that just as compression or tension produces an electrical effect in these cases, so electrification, in the same sense as that developed, produces a minute compression or extension. For the phenomena are reciprocal, a potential difference applied between the two faces perpendicular to the electric axis causing the crystal to expand along the electric axis and contract in a direction mutually perpendicular to the electric and optic axes, or *vice versa*, according to sign. Lippmann [1] was the first to observe this fact, and subsequently Kundt [2] showed that the effect is rendered evident by the alteration in the shape of the uniaxial optic axial rings observed in convergent polarised light, the circular rings becoming deformed into elliptical ones, just as produced by direct compression perpendicular to the axis. J. and P. Curie [3] have actually measured the compression suffered by quartz in a powerful electrical field.

The results which have already been obtained may perhaps best be summarised as follows, taking quartz as the typical crystal example, and assuming that a rectangular block has been cut out of the crystal with its longest dimension parallel to the optic axis and its shortest parallel to the electric axis of the crystal, the three pairs of parallel oblong faces being ground and polished true planes.

Three cases are to be distinguished, according to which of the three pairs of parallel faces are used.

Case 1.—The largest pair of faces are used, bounded by the longest and intermediate edges. (*a*) When a pressure is applied normally to these faces, that is, along the electric axis, and perpendicular to the optic axis, charges of positive and negative electricity develop on these two faces respectively, in accordance with the simple law expressed by the equation

$$Q = KF,$$

where Q is the quantity of electricity liberated, F is the force in dynes applied, and K is the piezo-electric constant of the crystal. The quantity of electricity liberated is found to be independent of the thickness t of the slab along the electric axis. If the quantity of electricity released per unit area A of one square centimetre be $q = \frac{Q}{A}$, and $p = \frac{F}{A}$ be the force per sq. cm., then $q = Kp$.

(*b*) If instead of compression a tension be applied, the same quantity of electricity is liberated, but the polarity is reversed.

(*c*) If equal quantities of positive and negative electricity are applied respectively to the two parallel faces in question, dilatation or contraction of the crystal occurs in the direction of the electric axis normal to the faces, and if the charges be reversed in sign, contraction or expansion, the inverse phenomena, will occur.

Case 2.—If the crystal block be compressed normally to the other

[1] *Ann. Chim. Phys.* (5), 1881, *24*, 145; *Journ. de Phys.* (1), 1881, *10*, 381.
[2] *Ann. der Physik*, N.F., 1883, *18*, 228.
[3] *Compt. rend.*, 1881, *93*, 1137; 1882, *95*, 914; also *Journ. de Phys.* (2), 1889, *8*, 149

long pair of faces (composed of the longest and shortest edges), that is, perpendicular to both the electric axis and the optic axis, there will result a liberation of electricity on the same faces as were used for case 1, but of opposite sign, the law being in accordance with the equation

$$Q = -K \cdot \frac{l}{t} \cdot F,$$

where t is again the thickness of the slab along the electric axis (shortest) and l is that along the intermediate dimension normal to both optic and electric axes.

Case 3.—If the block be strained along the direction of the optic axis, normal to the small end-faces, no liberation of electricity occurs, and no contraction or expansion accompanies the application of an electric field.

The value of the constant K, *i.e.* the quantity of electricity liberated per dyne, is found to be about $6{\cdot}5 \times 10^{-8}$ for quartz. Lippmann found that, as a consequence of the reversibility of cases 1 and 2, if a difference of potential V be applied to the block in the direction of the electric axis, the consequent dilatation or contraction is given by $\delta_1 = -KV$, while if it were applied in a direction perpendicular to the electric axis it would be $\delta_2 = +K \cdot \frac{l}{t} \cdot V$. Recent experiments have still further confirmed these rules, which are independent of t, so that $\frac{\delta_1}{t} = -K\frac{V}{t}$, and electric stress $= -\frac{1}{K}$ (mechanical strain), or $\frac{\text{stress}}{\text{strain}} = -\frac{1}{K}$, just as $\frac{\text{stress}}{\text{strain}} = E$ in mechanics (E being Young's modulus).

The value of $\frac{1}{K}$ is $1{\cdot}5 \times 10^7$ for quartz, and may be called the piezo-electric modulus. For the law is clearly equivalent to Hooke's law, which states that elongation is proportional to the force producing it, the stress being the stretching force and the strain the temporary elongation.

The mechanical strains in cases 1 and 2 for any dimensions of the slab are the same for a given electric stress. If p = mechanical stress and E be the modulus of elasticity, we obtain

$$p = E \times \text{strain} = E \times \frac{\delta}{t}$$

$$= E \cdot K \cdot \frac{V}{t} = M \cdot X,$$

where X is the electric field in electrostatic units.

Thus, although the expansion or dilatation depends on the potential difference only, the mechanical stress produced is dependent on both V and t.

Considerable ingenuity has been displayed in utilising these facts, especially those concerning quartz, during the Great War, all of which have been fully confirmed in the course of the thorough investigation which has been involved, and the author is indebted to Mr. Reginald E.

Gibbs, of University College, London, who took part in the work, for the concise summary afforded in the later part of this section, and to the Lords of the Admiralty for their kind permission to include this contribution. The piezo-electric charges are used in France to measure small charges by means of a balancing method, which admits of great accuracy. Sir J. J. Thomson in this country has used the charges developed to deflect his "nimble electrons," in such a manner that a continuous record of the change of pressure during explosions can be recorded.

As regards the piezo-electrical properties of Rochelle salt, $C_4H_4O_6KNa \cdot 4H_2O$, which crystallises in the rhombic bisphenoidal class 6, it has recently been shown by A. M. L. Nicolson [1] that the piezo-electrical activity is best produced by static compression, the application of torsion, or by desiccation. Of all the causes studied a twisting couple about the principal axis was found to excite the greatest potential difference between the electric poles. According to Hankel and Lindenberg,[2] either by cooling or by pressure the faces of the form {111} become negatively electrified, and those of {1$\bar{1}$1} positively. The four electrical axes are consequently parallel to the normals to the faces of these two forms.

Voigt [3] and also Pockels [4] have given theories connecting all these facts, especially those of pyro- and piezo-electricity, with the elastic, electrical, optical, and dielectric constants of crystals, for which it is desirable that the original memoirs should be consulted, as the present state of the subject is far from either satisfactory or complete. Indeed a most promising field of research is offered by the subject, the fringe of which only has yet been touched. The Interference Apparatus for general use in Fine Measurement, which is being constructed for the author as described in Chapter LVIII. (pages 1358–1364), should prove particularly suitable for determining the small amounts of compression or extension occurring in these piezo-electrical experiments, and it is the author's intention to use it for further work on this subject.

The fact that the changes of volume on electrification are instantaneous, rendering the counting of half wave-length interference bands furnished by the crystal itself impossible, will be no drawback with this instrument, as the movement can be followed up at leisure, and the bands deliberately counted the while, by the very fine-movement microscope; for this itself carries the movable black glass disc which furnishes one of the two interference surfaces. The fiducial mark on, or travelling with, the end of the crystal which is to be observed by the microscope, will be a Grayson-ruling signal as described on page 1358, and the operation will simply consist in following the movement of this fiducial mark (itself of only wave-length dimensions), and of counting the bands corresponding to the travel of the microscope between the two positions occupied by the mark before and after electrification of the crystal.

Magnetic Induction.—When a small bar of a solid substance is suspended

[1] *Proc. Amer. I.E.E.*, 1919, *38*, 1315.
[2] *Zeitschr. für Kryst.*, 1897, *27*, 515.
[3] *Abh. Ges. der Wiss.*, Göttingen, 1890, *36*: *Ann. der Phys. und Chem.*, N.F., 1895, *55*. 701.
[4] *Neues Jahrbuch für Min.*, 1890, *7*, 253.

by a silk thread horizontally, and free to turn in the horizontal plane, between the two poles of a powerful electromagnet, it becomes affected by induced magnetism, and its two ends are either attracted or repelled by the two poles of the magnet. If the substance be capable of itself exhibiting the properties of a magnet, such as iron, nickel, cobalt, or a salt of one of these metals, or even a glass containing one of them in its composition, it is said to be "paramagnetic," and the position which the bar takes up after a certain amount of oscillation is an axial one, that is, the length of the bar is parallel to the line joining the two poles of the magnet. The magnetic field in this case is stronger in the substance than in the air around it, owing to the "permeability" to induction being greater than for air. Fig. 921 will render the nature of the experiment clear.

If, however, the substance be not one capable of exercising magnetism like iron, the bar will set itself between the poles of the magnet equatorially, at right angles to the line joining the poles, and the substance is said to be "diamagnetic." In this case, which is that actually shown in Fig. 921, the permeability to magnetic induction, and therefore the magnetic field in the substance, is feebler than that in the air surrounding it.

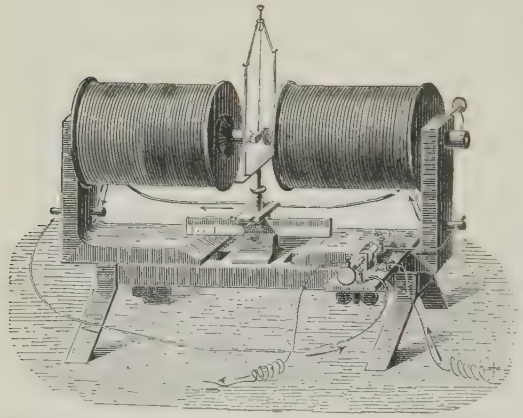


FIG. 921.—Apparatus for Determining Para- or Diamagnetism.

In the case of the more permeable, paramagnetic substance, the so-called "tubes of force" of the inducing field crowd into the substance from the outside air, and become more widely spaced in the air around. On the other hand, the tubes of force become fewer in the diamagnetic body than they were in the air around, into which they pack themselves more closely than when the body was not there.

The introduction of a diamagnetic body into a magnetic field is followed by induction similar to when a paramagnetic body is introduced, but the induced poles are oppositely orientated to their direction in a paramagnetic body. In a diamagnetic body the induction through the body is less than the value of the field which would exist if the body were not present. The tubes of force due to the (dia)magnetism induced in the body run within the latter in the opposite direction to the tubes of force of the inducing field. A north pole, for instance, the place where the tubes of force leave the body, is formed at that end of the body which is turned towards the direction from which the tubes of force of the outside field enter the body.

The extent or power of the diamagnetism induced in bodies behaving diamagnetically is very much smaller than the magnetism of iron, nickel, or cobalt. Bismuth is the most strongly diamagnetic substance known,

but its permeability is only 0·9998 compared with the paramagnetic permeability of iron of 2000.

If a sphere of an amorphous substance, whether it be paramagnetic or diamagnetic, be suspended between the poles of the magnet, instead of a bar, there is no tendency for it to alter its natural position of rest, as its dimensions are equal and its internal structure is similar in all directions; it behaves thus as magnetically isotropic. Crystals, however, in general behave differently, for the property of magnetic induction resembles the other physical properties which have been dealt with in exhibiting different intensities, or facilities for permeability, in directions which are different with respect to the symmetry. The property, indeed, is one of vectorial quality, for the values are represented by an ellipsoid with three rectangular axes, the Ellipsoid of Magnetic Induction, which becomes simplified to an ellipsoid of revolution for the three uniaxial systems (trigonal, tetragonal, and hexagonal), and to a sphere for crystals belonging to the highly symmetrical cubic system. The directional effect can be eliminated, however, and the crystal tested like an amorphous body simply for para- or diamagnetic properties, by powdering the crystal and placing the powder in a small and very thin-walled glass tube so as to fill it. The particles having every possible crystallographic orientation, the effect of crystallisation is eliminated, and the tube sets itself between the magnet poles either axially or equatorially, according as the substance of the crystal is para- or diamagnetic.

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Singly refractive crystals, that is, those belonging to the cubic system, behave like glass or other amorphous material, in receiving equal para- or diamagnetic induction in all directions, and therefore a sphere cut out of the crystal takes up no specific position between the magnet poles. It is not even necessary to powder the crystal and apply the test for para- or diamagnetism to the powder enclosed in a tube, a bar can be used cut directly from the crystal, and the observation made as to whether it sets itself axially or equatorially.

Uniaxial doubly refractive crystals (trigonal, tetragonal, or hexagonal) take up the strongest para- or diamagnetisation either along the axis or in all directions perpendicular thereto. If the maximum be parallel to the axis and the minimum perpendicular thereto, the crystal is said to be positive; if the reverse be the case, the axis being the direction of minimum effect, the crystal is termed negatively magnetic. If a sphere be turned out of such a crystal it will only remain unaffected as regards position between the magnet poles when it is hung up so that its trigonal, tetragonal, or hexagonal axis is vertical. If it be otherwise suspended, however, it will take up a definite position, which was shown by W. Thomson [5]

[1] *Pogg. Ann.*, 1847, *72*, 315; 1849, *76*, 576, and *77*, 447; 1850, *81*, 115; 1851, *82*, 42.
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[4] *Sitz. Ber. Wien. Akad.*, 1858, *32*, 43.
[5] *Brit. Assoc. Reports*, 1850, Part ii. 23; *Phil. Mag.*, 1851, *1*, 177.

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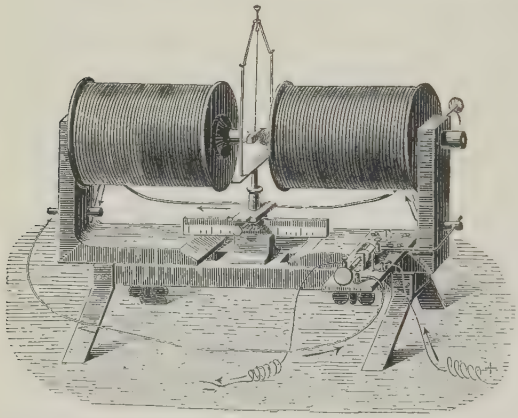

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(Lord Kelvin) to be dependent on the strength of the magnetic field, the values of the two principal coefficients of magnetisation of the crystal (parallel and perpendicular to the axis) and the crystal orientation. Measurements carried out with spheres of calcite agreed perfectly with his theory. If the sphere be suspended with the axis horizontal, and the crystal be paramagnetic and positive, the sphere sets itself so that the direction of the optic axis is axial, but when the axis is the minimum magnetic axis and the crystal is negative, the sphere sets itself so that the direction of the axis becomes equatorially arranged. The reverse occurs in each case when the crystal is diamagnetic. A cube sets itself similarly definitely when one pair of faces are at right angles to the optic axis, and it is suspended with this axis horizontal.

The results for some of the uniaxial substances investigated were as follows: Chalybite, carbonate of iron $FeCO_3$, proved, as might be expected from a salt of iron, to be positively paramagnetic; it crystallises in the trigonal class 21, like calcite. Calcite $CaCO_3$ and sodium nitrate $NaNO_3$, likewise trigonal of class 21, and also wulfenite, lead molybdate $PbMoO_4$, which is tetragonal of class 9, all revealed themselves as positively diamagnetic. Tourmaline (trigonal of class 20), beryl $Be_3Al_2(SiO_3)_6$ (hexagonal of the holohedral class 27), dioptase H_2CuSiO_4 (trigonal of class 17), and hexahydrated nickel sulphate $NiSO_4\ 6H_2O$ (tetragonal of class 11) were all found to be negatively paramagnetic; and bismuth, antimony, arsenic (all three trigonal of class 21), ice (hexagonal of class 25), and zircon (tetragonal of the holohedral class 15) exhibited negative diamagnetic properties.

Biaxial doubly refractive crystals (rhombic, monoclinic, or triclinic) possess three different principal coefficients of magnetisation in three mutually perpendicular directions, the axes of the magnetic induction ellipsoid. As such a surface has two circular sections, there are two planes in which such crystals take up equal magnetisation. If a sphere be cut out of a biaxial crystal, therefore, and suspended between the two poles of the electromagnet, with the normal to either of these two planes vertical, the sphere behaves like an isotropic one. The two normals to these two planes are termed the magnetic axes, and the crystal is thus magnetically biaxial as well as optically so. When the sphere is hung in any other manner, it takes up some definite position, which in all cases is one in which that direction in the plane of possible rotation which takes the strongest paramagnetisation, or the weakest diamagnetisation, becomes axially arranged with respect to the two magnet poles.

In the cases of crystals in which the directions of the axes of the optical ellipsoid are identical for all colours, that is, those of the rhombic system, the three axes of the magnetic ellipsoid also coincide with the crystallographic axes. If a cube be cut from a rhombic crystal so that its three pairs of parallel sides are perpendicular to these three axes, and it be suspended between the magnet poles so that one of the three axes is vertical, the pair of faces perpendicular thereto being then horizontally arranged, the cube will set itself so that one of the other two pairs of faces are axially arranged and the other (third) pair equatorially; which particular pair is

axial and which is equatorial depends naturally on the para- or diamagnetic nature of the substance, and on the quantitative relationship of the induction along the two normals to the two pairs of faces. Suspension parallel to each of the other two axes in turn will afford two other sets of observations, and the combination of all three will afford the necessary information as to which axis is the maximum, which is the minimum, and which is the intermediate axis of magnetic induction.

For instance, suppose a rhombic crystal has shown itself to be paramagnetic by the powder test, and that on hanging up the crystal by the three crystallographic axial directions in turn the following observations are made :

Direction of Suspension.	Direction which sets Axially.	Direction which sets Equatorially.
Axis *a*	Axis *b*	Axis *c*
,, *b*	,, *a*	,, *c*
,, *c*	,, *b*	,, *a*

The magnetic induction is thus strongest in the direction of axis *b*, which has set itself twice axially, and weakest along the vertical axis *c*, which has twice arranged itself equatorially, *a* being the intermediate axial direction of the magnetic ellipsoid. If, however, the character had proved itself to have been diamagnetic on applying the powder test, the direction *c* would have been the maximum and *b* the minimum axis of the magnetic ellipsoid.

Plücker termed those crystals positive for which the acute angle of the magnetic axes is bisected by the greatest induction axis, and those negative for which the bisector is the axis of least magnetic induction.

A number of rhombic substances have been investigated by Grailich and von Lang (*loc. cit.*), among them being potassium sulphate K_2SO_4, ammonium sulphate $(NH_4)_2SO_4$, and potassium chromate K_2CrO_4. Potassium and ammonium sulphate proved to be diamagnetic, and for each salt the axis *b* was found to be the maximum, the axis *a* the minimum, and the axis *c* the intermediate axis of magnetic induction.

In the case of monoclinic crystals, one axis only of the magnetic ellipsoid is identical with a crystallographic axis, the symmetry axis *b*, and the other two lie mutually perpendicular somewhere in the symmetry plane. Their direction is determinable by suspending the crystal with the symmetry axis vertical. The two magnetic axes also lie in the plane of symmetry, which is horizontal and free to rotate when the crystal is thus suspended, if the two axes of the ellipsoid which arrange themselves axially and equatorially are the maximum and the minimum axes ; but the magnetic axes lie in a plane perpendicular to the symmetry plane if one of the set directions be the intermediate axis. Plücker found the monoclinic crystals of diopside, $CaMg(SiO_3)_2$, and potassium ferrocyanide, $K_4Fe(CN)_6$, to be paramagnetic, and those of sodium acetate, $NaC_2H_3O_2 . 3H_2O$, to be diamagnetic.

If the crystal be triclinic the three rectangular axes of the magnetic ellipsoid have no relation to the chosen crystallographic axes, and must be sought for by experiment. Plücker investigated the triclinic crystals of copper sulphate, $CuSO_4 . 5H_2O$, potassium dichromate, $K_2Cr_2O_7$, and cyanite (disthene), Al_2SiO_5. In the case of the last-mentioned substance the interesting observation was made that the crystal at once took up a definite position under the influence of the earth's magnetism, as soon as it was suspended by the silk thread, and before the magnet was actuated.

A few crystalline minerals retain their magnetisation permanently, particularly the important triferric tetroxide, magnetite,[1] Fe_3O_4, which crystallises in the holohedral class 32 of the cubic system, and magnetic pyrites, pyrrhotite, the composition of which is FeS + a little excess S (corresponding approximately to Fe_nS_{n+1}), which crystallises hexagonally, either truly in that system or in the rhombic system with pseudo-hexagonal habit. Doubtless the magnetisation has been induced by the earth's magnetism. In the case of the isotropic (cubic) magnetite the permanent magnetism is exhibited in all directions, and in those cases where magnetite crystals are found to possess one or more north and south-seeking poles, their position bears no relation to the crystal structure, the perfect symmetry causing them to behave in this respect just like iron or steel, in which the structure is microcrystalline with the crystals arranged in all kinds of orientations. In the case of the apparently hexagonal pyrrhotite, the crystal only remains permanently magnetic in directions perpendicular to the axis.

An excellent mathematical discussion of the theory of magnetic induction in crystals of W. Thomson (Lord Kelvin), and an account of its experimental confirmation for calcite by Stenger and König, are given by Liebisch in his *Physikalische Krystallographie*, pages 196-214.

In concluding this chapter reference should be made to the results of a highly interesting research by A. E. Oxley on Magnetism and Atomic Structure, which were described at the meeting of the Royal Society on November 18, 1920.

From Tyndall's work and these experiments of Oxley, on the characteristic deportment of diamagnetic and paramagnetic crystals in the magnetic field, it appears that in non-ionised crystal structures the fundamental unit of the space lattice is the molecule. It was shown that the electron orbits in atoms must be distributed in space round the nucleus, each electron describing a small orbit, or alternatively the electron itself

[1] It is to the natural permanent magnetism of magnetite, the "lodestone," *magnes lapis*, that the Science of Magnetism owes its name. Whether the origin of the name of the mineral itself is due to the discovery in very early times of considerable quantities of the mineral at Magnesia in Asia Minor, or whether there be solid fact behind the remarkable story told by the elder Pliny in his *Natural History*, that a shepherd of Mount Ida named Magnes discovered the lodestone, by having his shoe nails and shepherd's staff attracted forcibly to it, and that the mineral came thereafter to be named *magnes lapis* after the shepherd, does not appear to be ever likely to be cleared up, although the former origin is more generally credited. It was not until the tenth century that the term "lodestone" (meaning leading stone) came into use, after the discovery that a suspended slab of the mineral arranged itself north and south and thus became of great use in navigation.

may be a complex unit endowed with magnetic properties. In either case the distribution must be such that the aggregate projected area of the electron orbits on a plane perpendicular to the principal cleavage is a maximum both in diamagnetic and paramagnetic crystals. This result is consistent with a closer packing of the molecules in a direction parallel to the principal cleavage. In crystals of the simple cubic form X-ray analysis has indicated that the structure is or resembles an ionised-atomic one, and the cleavages are all of equal value. Such crystals show no appreciable structural deportment in the magnetic field.

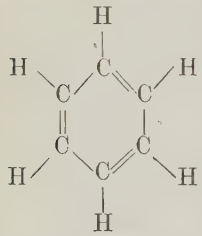
The above views of Oxley relating to electron distribution are consistent with the cubical atom theory of Lewis and Langmuir, but not with Bohr's theory. The coupling forces between atoms and molecules in non-ionised crystals are due to the mutual magnetic induction between pairs of electron orbits. A model of the hydrogen molecule is suggested in which the arrangement of the coupling units determines a diamagnetic molecule as required by experiment.

It is considered that the above views and those of Bohr may eventually be brought into line by a fuller recognition of the possible differences between radiating and non-radiating matter.

CHAPTER LX

"LIQUID CRYSTALS"

REFERENCE has several times been made during the course of this book to the so-called "liquid crystals" discovered by Reinitzer in the year 1888 and so ably worked out by Lehmann,[1] and although the theory concerning their nature is still a matter of discussion and more or less of controversy, there can be no question about the fact of the existence of substances certainly liquid, which exhibit some of the attributes of crystals, especially double refraction and dichroism. The substances are chiefly compounds of carbon, and mostly derivatives of benzene C_6H_6 containing a large number of atoms, and often derivatives of that hydrocarbon in which the replacement of two hydrogen atoms of the benzene ring has occurred in the "para" position, that is, at two opposite points in the hexagonal ring, thus conferring on them, as the replacing groups are themselves also complicated, an elongated and more or less rectilinear configuration. One of the most prominent of the substances not aromatic in their nature is the ammonium salt of oleic acid, $C_{18}H_{34}O_2$, a very long and straight chain compound belonging to the unsaturated series of fatty acids. Vorländer,[2] who discovered several of these substances (and has more recently prepared many more), which were afterwards studied further by Lehmann, has shown that this extended chain-like character is one of the most favourable conditions for the production of "liquid crystals." Also they are generally substances which exist in solid crystalline condition at the ordinary temperature, and after fusion above their melting-point form, on partial cooling, with more or less turbidity, at a specific temperature, a second modification consisting of "liquid crystals."



Benzene.

The discovery of the fact that these substances produce crystal-like bodies, when examined under the microscope at certain particular temperatures, came about as a side issue from the work of Lehmann on chemical reactions under the microscope at higher temperatures. His heating microscope is now a well-known instrument, and one form of it,

[1] *Flüssige Krystalle*, Leipzig (Engelmann), 1904; *Zeitschrift für physikalische Chemie*, 1910, *71*, 355.

[2] *Ber. der Deutsch. Chem. Ges.*, 1907, *40*, 1970; 1908, *41*, 2033.

constructed by the firm of Steeg & Reuter (formerly Voigt & Hochgesang), has been described in Chapter LII. (Fig. 842, page 1172).

An excellent form of this microscope, as constructed with recent improvements by Zeiss, was also mentioned and illustrated in Chapter LII. and is shown in Fig. 922. It can be employed equally well for ordinary eye observation and for screen demonstration, the eyepiece, shown separately at A in Fig. 922, being removed when the instrument is required for the latter purpose, and the mirror fitting shown at the top of the instrument placed in position instead. Adjustment of the mirror for azimuth is afforded by rotation of the inner tube (to which its collar is attached) within the optical tube. Its altitude tilt may be regulated by means of a hinge, and its position fixed, after adjustment of the projected screen picture, by means of a tightening screw. The best Zeiss microscope is at once adapted for the purpose by making certain additions to its ordinary equipment. Firstly, the microscope-slip, which is somewhat wider than the usual 3 by 1 inch slip, is raised from the ordinary stage by means of eight little columnar supports. Two other pairs of little columns, insulated in this case, are arranged with holes and capstan screws to form binding screws for the attachment of electric wires, in the event of the action of the electric current on the substance on the slide being desired to be studied. Secondly, an adjustable miniature Bunsen burner is provided (seen on the left in Fig. 922), which can be swung under the centre of the stage, where the latter is open, and its flame may be regulated from the minutest size to that of a jet nearly an inch high ; the flame can, moreover, be converted into a blowpipe one if desired, as provision is also made of an air-blast attachment, both gas and compressed air from a weighted gas-holder being delivered by caoutchouc tubing to two little tubulures carried by a cylindrical mixing chamber. Both gas- and air-blast can be delicately controlled by means of a long lever gas-tap moving over a graduated arc, and by use of this it is possible

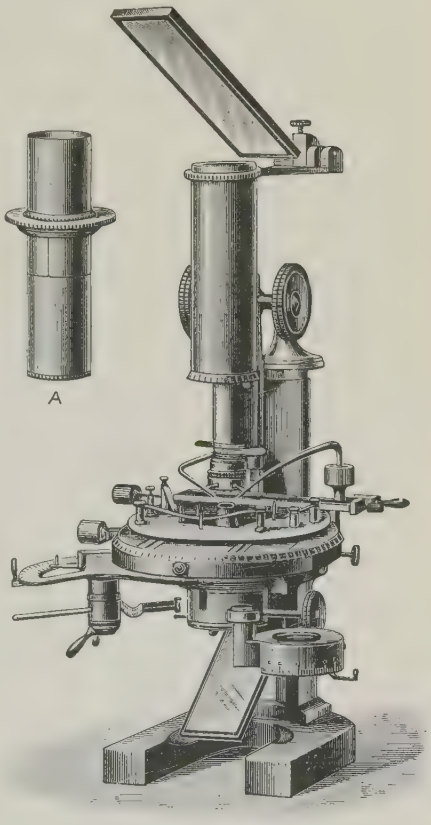


FIG. 922.—Lehmann's Heating Microscope as constructed in its latest Form by Zeiss.

to attain a constant temperature at any height up to 700° C. for quite a considerable time.

Thirdly, a means of rapidly cooling the substance on the slide, after it has been heated by the Bunsen flame, is provided, in the form of a couple of air-blasts, delivered from above by two equal tubes adjustable about ball-and-socket joints, one on each side of the stage, and directed down on to the slide. The compressed air is evenly supplied to both, so that the cooling effect on each side of the centre may be arranged to be quite equal. These are the three main attachments. Subsidiary fittings are : a water-jacket for the protection of the objective and of the analysing Nicol prism, fitted with tubulures for the delivery of a stream of cold water and its removal after circulation ; the mirror-fitting already alluded to for demonstration purposes, to direct the rays proceeding from the objective (used without eyepiece for screen demonstration) to the screen, and certain further protective arrangements, such as a convex screen, which may be fitted if desired round the optical tube just above the objective.

The most useful objective is the Zeiss 8-millimetre, magnifying without eyepiece about 30 diameters, and with the lowest-power eyepiece about 200 diameters. This objective serves admirably for the screen projections, the light from the electric lantern, in the form of a somewhat narrow parallel beam, being first directed into the microscope by the ordinary sub-stage mirror, and then concentrated on the object by the sub-stage condenser, and subsequently directed to the screen by the upper mirror attached for the purpose.

The originating discovery of Reinitzer in the year 1888 was that cholesteryl benzoate, after melting at its fusion point 140° C., changes to a turbid liquid, which is doubly refractive and remains so on further heating until it reaches the temperature of 179° C., when it suddenly becomes isotropic. This new fact was followed by the observation of Gattermann in 1890 that similar phenomena occur in the case of para-azoxy-anisol and para-azoxy-phenetol. After further substances of like character had been described by Vorländer, the subject was vigorously taken up by O. Lehmann, who considered that the phenomenon was due to the formation of crystals in the liquid condition, which appear perfectly transparent under the microscope. The turbidity which usually accompanies the phenomenon he attributed to the individual crystals being differently orientated, and thus scattering the light to a greater or less extent. Vorländer not only agreed with this view but asserted energetically that the substances were truly liquid crystals possessing a space-lattice structure. At the other extreme, however, G. Tammann expounded the view that these anisotropic liquids are merely emulsions of a particularly persistent character, but he entirely failed to account for the undoubted exhibition of double refraction, dichroism, and other optical properties characteristic of crystals, such as, in some cases, rotation of the plane of polarisation. Tammann's view will be shown in the sequel to have been quite untenable, in view of the large accumulation of experimental evidence to the contrary. On the other hand, the original view of Lehmann, and that of Vorländer, that these substances are true crystals, which involves a space-lattice

structure, will be shown also to be untenable, at any rate as going much too far, and it is understood that Lehmann himself does not now go to this length, and does not insist any longer on a space-lattice structure, although this is still maintained by Vorländer. Before proceeding further with attempts to account for the phenomenon, however, it is desirable to give a few further details concerning it.

In the year 1900 it was observed by Lehmann that these anisotropic liquids are influenced by being placed in a magnetic field, the molecules or their groups becoming all arranged similarly with respect to their axes, the turbidity disappearing and the liquid becoming quite clear. This fact was subsequently confirmed by E. Bose, who made the assumption that the

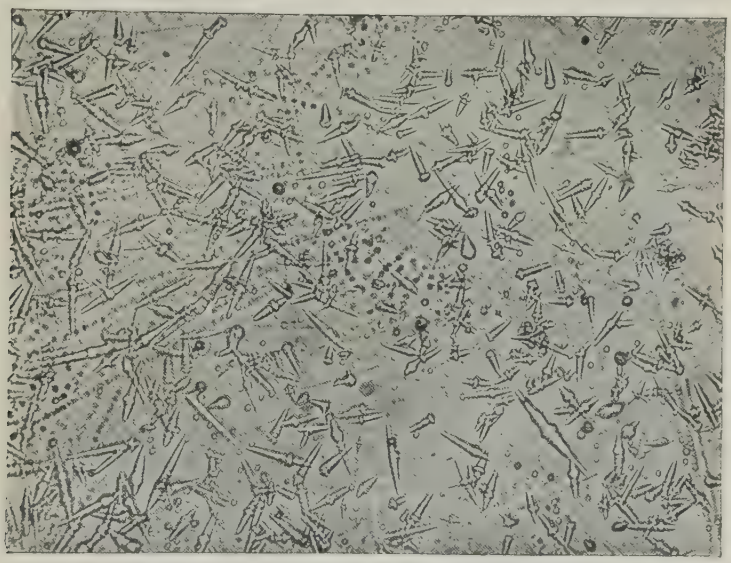


FIG. 923.—" Liquid Crystals " of Ammonium Oleate.

molecules are ellipsoidal, while Lehmann considered that the evidence pointed to a lamellar structure. In either case, the molecules appeared to set themselves in a definite position between the glass micro-slip on which the drop was placed and the cover-glass, the long axis of the Bose ellipsoid, or the plate surface of the Lehmann lamella, being set up perpendicularly to the glass surfaces, under the influence of the magnet. Under these circumstances the liquid behaved like the substance of a uniaxial crystal.

One of the most interesting of the many substances now known to produce " liquid crystals " is ammonium oleate, $C_{18}H_{33}(NH_4)O_2$, which has already been referred to as a very long chain-like compound belonging to the fatty series of organic substances, exhibiting the elongated character of molecule like the para-benzene compounds also already alluded to. The " liquid crystals " of ammonium oleate are obtained at a temperature only slightly above the ordinary, by simply allowing a warm solution in alcohol

to cool. They approach the form of steep double pyramids, seen with crossed Nicols, as shown (from an actual photograph taken by Prof. Lehmann and most kindly sent by him to the author) in Fig. 923 and at *e* in Fig. 924. These drawings are after Lehmann, but his later writings and the actual photograph (Fig. 923) show that the real forms are much rounded and not nearly so definitely sharply pyramidal. That they are liquid is at once seen by merely touching the cover-glass which is laid over the crystallising drop of solution on the slide, for they immediately become distorted, but regain their shape on removal of the pressure. The bodies polarise strongly between crossed Nicols, and are obviously doubly refractive. When two such "crystals" approach each other they become blended at the point of contact, as shown at *a* and *b* in Fig. 924, and are gradually drawn into each other, as represented in the successive figures *c* and *d*, until they are merged into a single individual *e* exactly like each separately before their union, but of double the volume. When an individual is

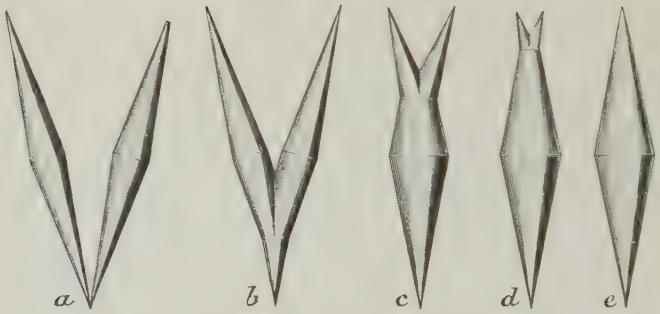


FIG. 924.—"Liquid Crystals" of Ammonium Oleate.

bent above a certain amount it either breaks, the two parts then becoming perfect smaller individuals, or it forms a knee-shaped twin.

The chief other substances which afford the phenomena of "liquid crystals" are para-azoxy-anisol, the esters of para-azoxy-benzoic acid and para-azoxy-cinnamic acid, para-azoxy-phenetol, cholesteryl benzoate, and cholesteryl acetate. The reproductions of two photographs of the ethyl esters of para-azoxy-benzoic acid and para-azoxy-bromocinnamic acid, kindly sent to the author by Prof. Lehmann, are given in Figs. 925 and 926.

Some of these, and of the numerous kindred substances now known to produce "liquid crystals" at specific temperatures, show formations which are apparently attempts at the production of prismatic crystals, more or less rounded at the edges, as in Figs. 925 and 926, while others exhibit the "liquid crystals" as spherical drops, showing double refraction in an unmistakable manner. In the case of some of the substances, such as para-azoxy-anisol, which form these spherical polarising drops, the drops may be set rotating independently by the addition of a little colophonium. Reproductions in Figs. 927 and 928 of two other photographs taken by Prof. Lehmann, of para-azoxy-anisol, show such drops very clearly and the effect of compression (between glass plates) on them, as seen under crossed

Nicols. In Fig. 929 the remarkable doubly refractive and dichroic streams of "liquid crystals" afforded in the case of dibenzal-benzidine are illustrated.

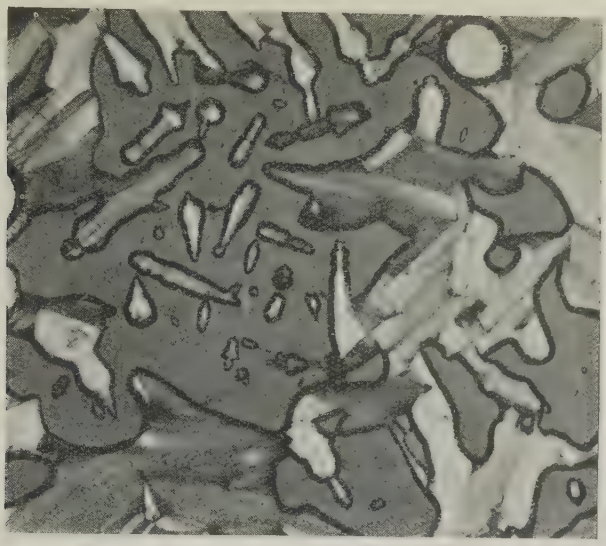


FIG. 925.—Ethyl Ester of Para-azoxy-benzoic Acid. Example of Prismatic "Liquid Crystals."

Generally, the substances are solids at the ordinary temperature. On melting under the heat of the little Bunsen flame they produce a non-polarising liquid, but on allowing this to cool, accelerated by gentle and carefully regulated use of the pair of cold-air blasts, at some particular temperature, corresponding, according to Lehmann, to the formation of a specific modification of the substance, the "liquid crystals" form, and if the temperature be then maintained constant they can be studied and photographed at leisure. On cooling further, however, the ordinary solid modification is again reproduced.

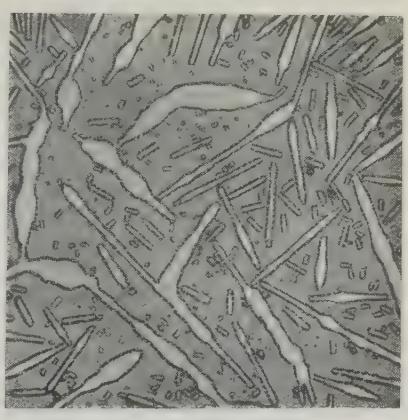


FIG. 926.—Ethyl Ester of Para-azoxy-bromocinnamic Acid. Example of Prismatic "Liquid Crystals."

A particularly beautiful example is afforded by the substance cholesteryl acetate, the chief beauty of the experiment consisting in the exquisite manner in which the solid form recrystallises on cooling from the anisotropic liquid stage. A slide is taken on which a very small quantity of the solid has been prelimin-

arily carefully melted, and the drop of liquid is then covered with a cover-glass After resolidification it shows under the microscope a confused

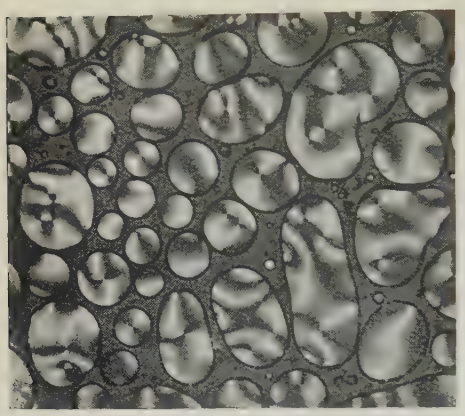


FIG. 927.—Dichroic "Crystal Drops" of Para-azoxy-anisol.

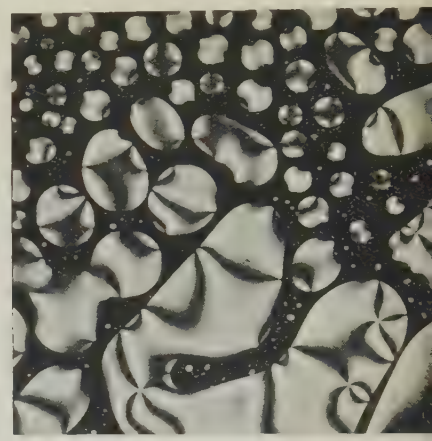


FIG. 928.—Spherical "Liquid Crystals" of Para-azoxy-anisol.

mass of radiating crystals of the ordinary solid variety. While still in position on the stage the little Bunsen flame is now brought underneath

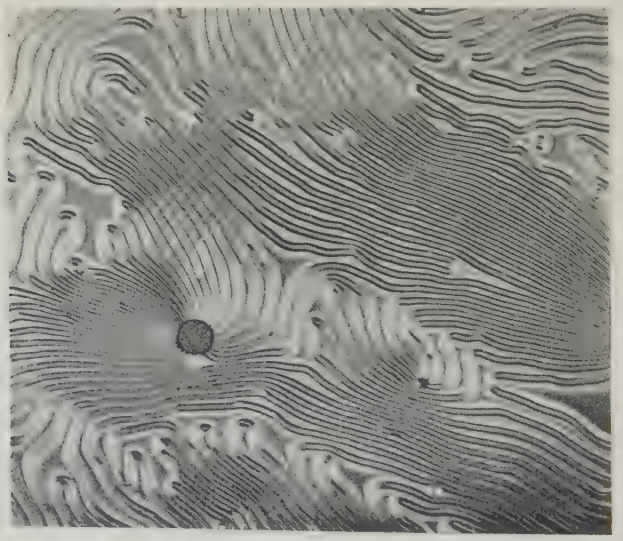


FIG. 929.—Streams of Elongated "Liquid Crystals" of Dibenzal-benzidine.

it until it again melts. The Nicols being crossed the field is practically dark, either to the eye, using the microscope in the ordinary way with an eyepiece, or on the screen when the eyepiece is removed and

the mirror substituted and the parallel beam from the electric lantern replaces the ordinary table microscope lamp. The Bunsen flame is then at once removed, and the two cooling air-jets above the stage allowed to play gently on each side of the centre of the slide. After two or three minutes, the Nicols being crossed for the production of the dark field, colour becomes visible, due to the double refraction of the "liquid crystal" modification which now forms. Presently, however, spherulites of the original solid modification commence to grow out of this brilliantly coloured liquid-crystal phase; small spots of light appear, probably in several places at once over the field, and rapidly develop into relatively large circular discs, of a pinkish to a yellowish colour, beautifully shaded both concentrically and radially, and strongly marked by a black cross parallel to the planes of vibration of the crossed Nicols. The field is soon almost covered with these beautiful apparitions, as if it were strewn with bright cruciferal flowers on a dark background, each one quite isolated if the cooling has been gradual, and the size never exceeding a moderate one, such as is represented in the typical field more or less faithfully reproduced, but with a lighter background, in Fig. 930. When the growth of these spherulites, somewhat flattened by the cover-glass, has become arrested, the remaining portion of the field is suddenly traversed by numerous radiating acicular crystals, also of the ordinary solid modification of cholesteryl acetate, but more rapidly formed from the labile state, polarising in brilliant colours and eventually completely filling the field.

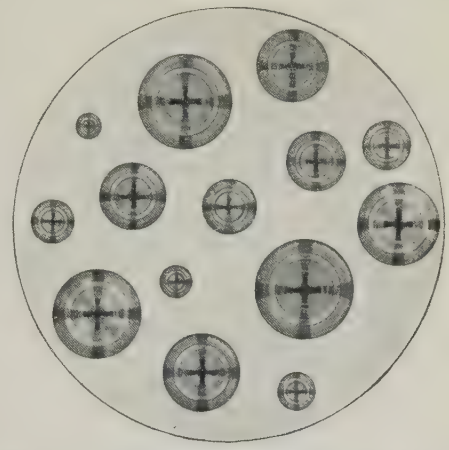


FIG. 930.—Spherulites crystallising out of the "Liquid Crystal" Variety of Cholesteryl Acetate.

Whatever be the truth concerning the nature of these much-discussed "liquid crystals" of Lehmann and Vorländer there can be no doubt of the reality of the phenomena, and that structures, probably of an intermediate character between the liquid condition and a true crystal, are built up by these long-chain molecules of the substances exhibiting the phenomena. There can be no getting away from the fact thus revealed that it is possible to these molecules, while forming a substance which is liquid—in some cases as mobile as water, although more frequently more or less viscous—to arrange themselves in some kind of primitive organised manner, akin to, but less perfect than, that in a crystal, and that when the "liquid crystals" are disturbed, or broken, they at once endeavour, usually with complete success, to recover their form and to repair the damage. It thus

appears that the molecules themselves, which are more or less free agents in the liquid condition, must be endowed with a directive force, a configuration-producing force, the " Gestaltungskraft " of Lehmann. In the cases of the bipyramids of ammonium oleate and of the prismatic forms of other substances producing " liquid crystals," the molecules would appear to arrange themselves almost as if the crystal were solid. In the spherical drops, however, they appear to take up a concentric arrangement.

Explanation of " Liquid Crystals."—The most rational explanation of the phenomenon of " liquid crystals " has been offered by Bose[1] in what has become termed his " Swarm Theory." It is based on the salient fact discovered by Vorländer that the molecules concerned are of exceptional length. The ordinary assumption of sphericity for a liquid molecule can certainly not be valid for a compound such, for instance, as anisaldazine, one of the substances forming " liquid crystals,"

$$CH_3O \cdot C_6H_4 \cdot CH : N.N : CH \cdot C_6H_4 \cdot OCH_3.$$

If two such elongated molecules approach so that the distance of separation of their centres of gravity becomes less than half their length, free rotation is arrested, except about the direction of their length, and a more or less parallel position is taken up by the two molecules. A bundle or " swarm " of such parallelwise arranged molecules will assume the symmetry of a rotation figure, and be likely to behave optically like a uniaxial crystal. Each swarm will be clear, but owing to the reflection and diffusion of light between the swarms turbidity will arise to a greater or less extent. Heating increases the molecular motion and thus diminishes the swarms, and when they become smaller than the wavelength of light the turbidity disappears and the liquid becomes clear.

Determinations of the viscosity of these anisotropic liquids at different temperatures, and investigations of their optical behaviour in a magnetic field, have afforded considerable evidence in favour of this swarm theory. The main idea is represented at *a*, *b*, and *c* in Fig. 931. At *a* is represented

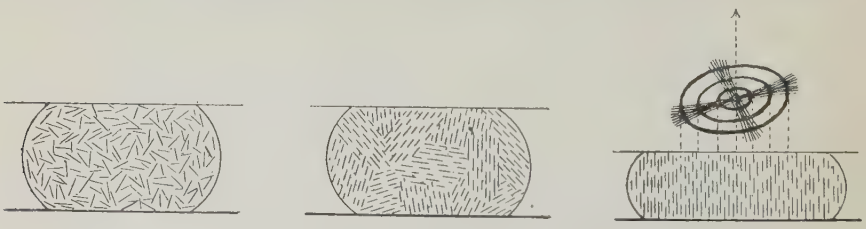


FIG. 931.—Bose's Swarms.

the promiscuous arrangement of the molecules in an ordinary isotropic liquid and in the liquids in question at temperatures superior to the clearing temperature ; *b* indicates the formation of swarms as the liquid cools below this temperature ; and *c* shows a single swarm, the molecules all

[1] *Physikal Zeitschr.*, 1907, *8*, 347 and 513 , 1908, *9*, 708 ; 1909, *10*, 32 and 230.

arranged end on when confined in the thin film between the micro-slip and the cover-glass, all parallel to themselves and perpendicular to the glass plates, an attitude which they readily take up, owing to molecular cohesion, and in which they afford the uniaxial figure in convergent polarised light.

The possession of the properties of dichroism, double refraction, and in some cases optical rotation, and the capability of affording an interference figure in convergent polarised light similar to that produced by a uniaxial crystal, while strong evidence of definite regularity of structure, do not necessarily indicate crystalline structure. The intermediate kind of structure assumed in Bose's swarm theory would be quite adequate to account for the phenomena observed. A still further consideration strongly pointing to the same conclusion is the fact that no biaxial interference figure has ever been observed to be afforded by any one of the fifty or more substances now known to form anisotropic liquids. As the vast majority of solid complex organic compounds crystallise in the optically biaxial systems of symmetry this fact is very significant as indicating the probability that the so-called "liquid crystals" are not crystals at all. No substances have been proved to yield anisotropic liquids except the complex long-molecule ones which have been referred to, chiefly para-aromatic and long-chain fatty compounds. The case of a simple binary inorganic compound, silver iodide AgI, is eliminated by the following considerations. This substance was supposed by Lehmann to exhibit the property of a "liquid crystal" at temperatures superior to 146° C., at which temperature it has been shown, on page 1328, to change from its ordinary hexagonal (dihexagonal pyramidal) form to a cubic variety. This supposition of liquidity has since been shown to be an error, due to impurity in the commercial salt; for when care is taken to purify it the substance remains quite as hard as yellow phosphorus up to 550°, within 2 degrees of the melting-point. The further fact that some of Vorländer's[1] more recent preparations of complex aromatic substances exhibit rotatory polarisation is explained readily by the swarm theory, for the molecules themselves are enantiomorphous. Likewise, the facts that the two indices of refraction, ω and ϵ, and the amount of optical rotation have been determined with some precision, do not carry us any further, for they are only the quantitative expression of the facts already explained by the swarm theory.

The question whether these anisotropic liquids possess the essential space-lattice structure of a true crystal would appear to be a suitable subject for decision by the new X-ray method of investigating crystal structure. Some preliminary experiments have been carried out in the laboratory of Prof. von Laue, by J. S. van der Lingen, with the substances para-azoxy-anisol, para-azoxy-phenetol, and anisaldazine, the result being quite negative, no evidence of such space-lattice structure having been afforded. Vorländer's contention, that the substances are truly liquid crystals possessing a space-lattice structure, on the one extreme, would thus appear to have been definitely negatived, just as Tammann's emulsion theory is out of the question on the other extreme. An arrangement of

[1] *Berichte der deut. Chem. Ges.*, 1908, *41*, 2033.

similarly orientated ellipsoidal molecules, with one axis only fixed in space, would account for all the phenomena of regularity of structure displayed. This would thus substantiate the views of Bose, or even to a large extent those of Lehmann, if one accepts as his latest view that what he terms "liquid crystals" are not dependent on a space-lattice structure, but merely on the specific properties of the molecules themselves, which enable them to arrange themselves in positions sufficiently definitely orientated to display double refraction, the property of growth in a suitable environment, and of exhibiting further definite orientation in a magnetic field.

Hence, it appears to be now established that the highly interesting anisotropic liquids are not liquid crystals properly so called. For they do not possess the fixed space-lattice structure which is the essence of a crystal, the true and perfectly organised solid. The parallelwise arrangement of the molecules, brought about largely by their inordinate length, and assisted in most cases by their degree of viscosity and the unusual play of molecular forces when the molecules are so elongated, attributes of the substances which are admitted by all who have studied them, would appear to constitute these remarkable bodies as a connecting link between ordinary liquids and true solid crystals. This conclusion, which does not apparently quite satisfy Lehmann, really renders these substances, which he has done so much to bring before us, more important and really more fascinatingly interesting than if his original view, that they were crystalline liquids, were substantiated.

Although many of Lehmann's theoretical conclusions have thus not been accepted, having been carried too far, yet besides the valuable results just indicated one further solid fact is obvious, namely, that the molecule possesses definite and even prominent individuality in these liquid bodies approximating in some degree to the nature of crystals, and forming a connecting link between true liquids and truly crystalline solids. Indeed, the inevitable outcome of Lehmann's work is that the molecular directive force concerned in crystallisation is re-established as a fact, after having been more or less discarded for a time as the effect of the results of the geometricians, who pushed their magnificent work beyond its true limits, and even more recently for a brief space after the announcement of the first results of the X-ray analysis of crystals. It had been assumed much too readily that no molecular directive force was concerned in crystallisation, because such a force was not absolutely necessary to account for the existence of a homogeneous structure; and that the mere mechanical fitting together, along the lines of greatest facility, of the structural units to form a particular kind of crystal structure, the ultimate units of which are the chemical atoms, was sufficient to account for that structure. The essential part of the splendid work of the geometricians is not at all affected by Lehmann's discoveries, the establishment of the 230 types of homogeneous structures possible to crystals standing as the great truth it undoubtedly represents, confirmed as it now is in a large number of cases by the actual location of the atoms by means of X-rays. But the mode of production of the particular type of structure in each individual case, and our ideas as to the *modus*

operandi of the act of crystallisation, are profoundly affected by this restoration to the molecule of its orientating directive force.

The importance of the space-lattice, as the expression of the fundamental molecular or polymolecular arrangement, in the case of the true solid crystal, is at the same time even further enhanced. For there can be no question but that a space-lattice arrangement of the molecules is the essence of true crystal structure, that of the perfect solid. It may possibly be constantly striven after and only very partially attained, in the cases of the bi-pyramidal and prismatic "liquid crystals" of such substances as ammonium oleate and the esters of para-azoxy-benzoic acid, although some of the substances exhibiting such forms are nearly as mobile as water; and the attainment of the intermediate parallelwise arrangement, the swarm, may be the result, the highest possible to a liquid, in the cases of these molecules of such relatively inordinate length. The directive molecular force may possibly and even probably be eventually traced to the negative electronic corpuscles composing, along with the positive nucleus, the atoms present in the molecule, and especially to the electrons of the outer shells of the atoms, as ultimate source. Much of the force is doubtless used up in inter-atomic attraction and repulsion, resulting in the stereometric arrangement of the atoms in the molecule, which gives rise on crystallisation to the particular Sohncke-Barlow point-system produced, determinative of the crystal class. Lehmann also suggests that astatic combinations are produced, which account for the negative results of crystallisation experiments in the magnetic field. For as Lehmann shows, such astatic molecules would endeavour to arrange themselves in space-lattices by reason of the considerable residual force (involving polarity in certain positions or directions) left after the maximum possible inner expenditure of energy had occurred. Whatever be the correct theoretical explanation, however, there can be no possible doubt about the fact that a directive force is at work endeavouring to produce and maintain a definite arrangement of the elongated and very complex chemical molecules of these remarkable liquids.

The definite experimental proof of the individuality of the molecule in the borderland between the truly liquid and crystalline states thus affords strong presumptive evidence that such individuality persists in the truly crystalline state.

This conclusion as to the reality of the molecular directive force renders many phenomena described by workers in the domain of crystallography relating to the deposition of crystals from solution or a state of fusion—notably Wulff and Sir Henry Miers, both of whom, as well as Lord Kelvin, have emphasised the prime importance of the molecular or polymolecular space-lattice—and which have been referred to in several chapters of this book, at once comprehensible, and it is in harmony with many facts also described by the author. It is also in full agreement with the results of the X-ray analysis of crystals, which have already proved the polymolecular character of the elementary cells of many space-lattices of well-known substances described in Chapter XXXIII., and even although, in the cases of the simplest of compounds, such as sodium chloride, the very simple

structure appears as if it were merely that of the "ions" of the elementary atoms present. Moreover, it was pointed out at the close of that chapter that there was a certain amount of definite evidence afforded of the persistence of the molecules, and therefore of intramolecular force, in the solid crystal state, and that this evidence was in keeping with a considerable accumulation of experimental facts derived from other branches of physics and physical chemistry.

It must now inevitably have been brought home to the reader how indissolubly the subject of crystallography is connected with the most important and fundamental of natural phenomena, and how deeply it concerns the student of natural science, whether he be devoting his energies to chemistry or to physics, or to their mutual borderland, physical chemistry. A study of the main facts of crystallography, such as have been brought together in this book, is indispensable to a right appreciation of any one of these three subjects.

The immense strides which crystallography has made during the last decade will be evident from the large amount of additional matter which it has been necessary to include in this second edition of the work, and from the fact that it has been necessary to extend it to two volumes. The author's wish, expressed in the concluding paragraph of the first edition, "that the near future might see many more keen and highly trained investigators taking up this fascinating branch of study, of such superlative importance to chemistry, and thus rapidly adding to the number of experimentally well-grounded and closely related facts," has thus already been to a large extent fulfilled, especially by the opening up of the highly promising new method of attack by means of X-rays. The future of the subject would thus appear to be assured, and the Science of the Perfect Solid, a Crystal, is bound to march ahead and to play its full part in the progress which is to follow the liberation of the colossal energies so lately, during more than four long years, devoted to War, and now happily free to turn to constructive, useful, peaceful pursuits, among which the most enthralling of all will undoubtedly be the further unravelling of the truly marvellous works of the Almighty in Nature.

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